

**SYNTHESIS, CHARACTERIZATION and PORE SIZE CONTROL OF
MESOPOROUS $\text{Li}_4\text{Ti}_5\text{O}_{12}$, CoTiO_3 and MnTiO_3 THIN FILMS**

A DISSERTATION SUBMITTED TO
THE DEPARTMENT OF CHEMISTRY
AND
THE GRADUATE SCHOOL OF ENGINEERING AND SCIENCE
OF
BİLKENT UNIVERSITY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF SCIENCE

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JULY 2014

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ABSTRACT

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July 2014

Salt-surfactant lyotropic liquid crystalline mesophases can be used to produce mesoporous highly transparent thin films of metal titanates. In this study, the salt-surfactant assembly is described as molten salt assisted self-assembly (MASA) process that was optimized for the synthesis of mesoporous CoTiO_3 , MnTiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin films with high specific surface area and narrow pore size distribution. The materials have been characterized using x-ray diffraction (XRD), Raman and UV-Visible absorption spectroscopy, Transmission Electron Microscopy (TEM), and nitrogen adsorption/desorption techniques. An initial clear solution containing two different surfactants ($\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$, $\text{C}_{12}\text{EO}_{10}$, and $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Br}$, CTAB), nitrate salt ($[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ or $[\text{Mn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ or LiNO_3) of the convenient metal, titanium(IV)butoxide ($\text{Ti}(\text{OC}_4\text{H}_9)_4$, TTB) as titania source and ethanol as solvent is prepared at an appropriate pH. Spin or spray coating methods was employed to coat the substrates using above solutions. During the coating process, a liquid crystalline mesophase is formed instantaneously upon the evaporation of the solvent. The hydrophilic surfactant domains guide the molten salt and hydrolysis products of TTB to form

a three dimensional porous network throughout the film. The synthesis is completed with a fast calcination step (10-20 min) at temperatures ranging between 350 °C to 550 °C.

Mesoporous CoTiO_3 , MnTiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ display uniform pores with a pore size of 25 to 55 Å, surface area of 193 to 445 m²/g and pore volume of 0.17 to 0.43 cm³/g depending on the composition and synthesis conditions. The surface area, pore-size, pore-wall thickness, pore volume and crystallinity of the pore-walls can be controlled by simply controlling the calcination or annealing steps of the process without damaging the mesoporous network. The films, produced by employing the MASA approach, are optically transparent and exhibit good adhesion on commonly used substrates (glass, silicon, aluminum... etc.). Both CoTiO_3 and MnTiO_3 are semi crystalline at low temperatures and undergo segregation into metal oxide and titania above 500 °C. However, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is nanocrystalline even at 350 °C and stable up to 550 °C. The initial calcination temperature and duration are two important parameters to further control the pore and crystallinity related properties in all three titanates.

The counter anion of the salt also plays an important role to adjust the porosity and to further modify. In this investigation, we also used the bromide salt of cobalt(II) and found out that one can incorporate graphitic carbon into mesoporous network. The MASA process, that is further expanded in this work, is not limited to metal titanates, investigated in this work and previous works; it is a general and new synthetic route to produce many other mesoporous metal oxides as powders, as well as thin films, such as LiCoO_2 , LiMn_2O_4 , etc...

Keywords: CoTiO_3 , MnTiO_3 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, mesoporous thin films, MASA synthesis.

ÖZET

MEZOGÖZENEKLİ $\text{Li}_4\text{Ti}_5\text{O}_{12}$, CoTiO_3 ve MnTiO_3 İNCE FİLMLERİN SENTEZİ, KARAKTERİZASYONU VE GÖZENEK BOYUTU KONTROLÜ

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Temmuz 2014

Tuz: yüzeyaktif liyotropik sıvı kristal fazlar, optik geçirgenliği oldukça yüksek mezogözenekli metal titanat ince filmlerin üretiminde kullanılabilir. Bu çalışmada, tuz ve yüzeyaktiflerin kendi kendine oluşumunu esas alan eriyik tuz yardımcı kendiliğinden oluşma (EYKO) prosesi; yüksek yüzey alanlı, homojen gözenek boyutu dağılımlı CoTiO_3 , MnTiO_3 ve $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ince filmlerinin üretimi için optimize edildi. Üretilen malzemeler x-ışını kırınımı (XRD), Raman ve UV-Görünür bölge soğurma spektroskopisi, geçirimli elektron mikroskopisi (TEM) ve azot adsorplama/desorplama teknikleriyle karakterize edildi. İki farklı yüzeyaktifin ($\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$, $\text{C}_{12}\text{EO}_{10}$, ve $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Br}$, CTAB), ilgili metalin nitrat tuzunun ($[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ ya da $[\text{Mn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ ya da LiNO_3) ve titanya kaynağı olarak titanyum(IV)bütoksit'in ($\text{Ti}(\text{OC}_4\text{H}_9)_4$, TTB) uygun bir pH'ta etil alkolde çözülmesiyle berrak çözelti oluşturuldu. Alttaşlar spin ya da spreyle kaplama yöntemleriyle bu çözeltiyle kaplandı. Kaplama esnasında çözücünün ani buharlaşmasıyla bir sıvı kristal faz oluştu. Yüzeyaktiflerin hidrofilik bölgelerinin rehberlik etmesiyle eriyik tuz ve TTB hidrolize ürünleri film boyunca uzanan 3 boyutlu bir ağ oluşturdu. Sentez, 350 ve 550 °C arasında değişen sıcaklıklarda yürütülen 10-20 dakikalık bir hızlı kalsinasyon adımıyla da son buldu.

Sentez koşulları ve kompozisyona bağlı olarak, elde edilen mezogözenekli CoTiO_3 , MnTiO_3 ve $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ince filmler; 25 ile 55 Å arasında boyutlara sahip düzenli gözeneklere, 193 ile 445 m²/g arasında yüzey alanlarına ve 0.14 ile 0.43 cm³/g arasında gözenek hacimlerine sahip olduğu belirlendi. Mezogözenekli yapıyı bozmadan; malzemenin yüzey alanı, gözenek boyutu, gözenek duvarı kalınlığı, gözenek hacmi ve gözenek duvarlarının kristallliği basit kalsinasyon ya da tavlama adımlarıyla kontrol edildi. EYKO yaklaşımıyla üretilen ve optik olarak şeffaf filmler, genel olarak sık kullanılan her türlü alttaşa (cam, silicon, alüminyum vs.) uygulanabilirliği gösterildi. CoTiO_3 ve MnTiO_3 'ün her ikisi de düşük sıcaklıkta yarı-kristal yapıda olup, 500 °C üstünde metal oksit ve titanya ayrışmasına uğradı. Fakat, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ 350 °C'de bile nanokristalin yapıda olup 550 °C'ye kadar yapısını korudu. Üç titanat malzemesinde de kristal ve gözenek yapılarını kontrol etmede, ilk kalsinasyon sıcaklığı ve süresinin önemli parametreler olduğu gözlemlendi.

Porozitenin ayarlanması ve değiştirilmesinde karşı anyonun da önemli bir role sahip olduğu ortaya çıkarıldı. Bu araştırmada, kobalt(II)'nin bromür tuzunun kullanımıyla yapıya grafitik karbonun da dahil edilebildiği saptandı. EYKO prosesinin sadece metal titanatlarla sınırlı olmadığı ve daha fazla genişletildiği bu ve eski çalışmalarımız da göstermiştir ki, bu yöntem LiCoO_2 , LiMn_2O_4 vs. gibi daha bir çok metal oksit tozların ve de ince filmlerin üretiminde yeni ve genel bir sentez yöntemidir.

Anahtar Kelimeler: CoTiO_3 , MnTiO_3 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, mezogözenekli ince filmler, EYKO sentezi.

Acknowledgement

I dedicate this work to my lovely parents (Hüseyin and Nurten Avcı) who were always there to provide me all kinds of moral and material support. I would like to thank Prof. Dr. Ömer Dağ not only for his excellent supervising in the project but also for the valuable and instructive conversations we shared about the philosophy of science. Also, special thanks to TÜBİTAK (112T407) for financial supports during my master studies.

Contents

1. INTRODUCTION	14
1.1. Porous Materials	14
1.2. Definition and Classification of Porous Materials	15
1.3. Mesoporous Materials	16
1.4. Soft-Templating for Non-Siliceous Mesostructures	17
1.5. Molten Salt Assisted Self Assembly (MASA) Synthesis of Mesoporous Metal Titanate Thin Films.....	19
1.6. Metal-Titanates	20
1.6.1. Literature on CoTiO_3	21
1.6.2. Literature on MnTiO_3	21
1.6.3. Literature on $\text{Li}_4\text{Ti}_5\text{O}_{12}$	22
2. EXPERIMENTAL PROCEDURE	24
2.1. The General Route for Sample Preparation.....	24
2.2. General Optimizations.....	25
2.2.1. Optimizations of the Amount of Concentrated Nitric Acid	25
2.2.2. Optimization of the Metal to Surfactant Ratio.....	25
2.2.3. Optimization of the Calcination Temperature	26
2.2.4. Optimization of the Calcination Time.....	26
2.3. Preparation of Powder CoTiO_3	26
2.4. Preparation of Powder MnTiO_3	26
2.5. Preparation of Powder $\text{Li}_4\text{Ti}_5\text{O}_{12}$	27
2.6. CoTiO_3 prepared using CoBr_2 as a cobalt source	27
2.6.1. Preparation of the samples and N_2 sorption measurements	27
2.6.2. Raman Spectroscopy.....	27
2.7. Sample preparation for TEM imaging.....	28
3. RESULTS & DISCUSSION.....	29
3.1. The Effect of acid on the mesophase and mesoporus CoTiO_3 thin films	29
3.2. Determination of the optimum metal salt to CTAB ratio.....	36

3.3.	Calcination of LLC Thin Films.....	42
3.4.	Control of Crystallinity and Pore Size of Mesoporous CoTiO_3 , MnTiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Thin Films via Post-Calcination Annealing.....	66
3.4.1.	Temperature Dependent XRD Measurements.....	67
3.4.2.	Temperature Dependent Raman Spectroscopy.....	71
3.4.3.	Temperature Dependent N_2 Sorption Measurements and Pore Size Control of Mesoporous Metal Titanates.....	75
3.4.4.	TEM Analysis of Mesoporous Metal Titanate Thin Films.....	84
3.5.	Effect of Direct Calcination vs. Step by Step Annealing on the Mesostructure	89
3.6.	Production and characterization of mesoporous metal titanate/graphite nanocomposite thin film.....	93
4.	CONCLUSION.....	99
5.	FUTURE WORKS.....	100
5.1.	LiMn_2O_4	101
5.2.	LiCoO_2	103
6.	REFERENCES	106

Figure 2.1 The general route for sample preparation	24
Figure 3.1. The XRD patterns of the as-prepared samples with different amount of acid (as marked in the patterns with a colour code), low amounts.....	29
Figure 3.2. The XRD patterns of the as-prepared samples with different amount of acid (as marked in the patterns with a colour code), high amounts.....	30
Figure 3.3 OM image of a) a sample containing less than 200 mg of acid and b) more than 300 mg of acid.....	31
Figure 3.4 N ₂ (77.4 K) sorption isotherms of both samples prepared using 50 mg and 500 mg of concentrated HNO ₃	32
Figure 3.5 The pore size distribution of both samples prepared using 50 mg and 500 mg of concentrated HNO ₃	32
Figure 3.6 The UV-visible spectra of mesoporous CoTiO ₃ thin films prepared using (a) 500, (b) 600, and (c) 700 mg of concentrated HNO ₃	34
Figure 3.7 SEM micrograph of sample prepared using a) 500 mg and b) 800 mg of concentrated nitric acid c) and d) magnified images of panel a) and b) , respectively.....	36
Figure 3.8 The small angle XRD patterns of samples, prepared using different amount of salt (as marked, salt:surfactant mole ratio).....	37
Figure 3.9 XRD patterns of 3 samples prepared with different amount of salt.	39
Figure 3.10 The behaviour of the mesophase upon the increase of the salt:C ₁₂ EO ₁₀ ratio.	40
Figure 3.11 The small angle XRD pattern of the as-prepared sample using 4:4:1 Co:Ti:C ₁₂ EO ₁₀ molar ratio.	41
Figure 3.12 GISAXS pattern of the as-prepared sample using 4:4:1 Co:Ti: C ₁₂ EO ₁₀ molar ratio.....	42
Figure 3.13 Visible absorption spectra of Co(II)-Ti(IV) sample at different temperatures (as marked).	44
Figure 3.14 Raman spectra of Co(II)-Ti(IV) sample at different temperatures	45
Figure 3.15 Time dependent XRD patterns of the as-prepared sample with 4:1 salt:C ₁₂ EO ₁₀ ratio.....	47
Figure 3.16 OM image showing the crystal growth of the salt species (circled in red).....	48
Figure 3.17 Photograph of a transparent vs. opaque film.	49
Figure 3.18 Raman spectra recorded from the surface of CoTiO ₃ films calcined for 7 hrs and 5 min.50	
Figure 3.19 Raman spectra recorded from the scraped powder of CoTiO ₃ samples calcined for 7 hrs and 15 min.....	51
Figure 3.20 Raman spectra collected from the surface of the samples prepared with different amount of acid.	52
Figure 3.21 Raman spectra collected from the powder form of the samples prepared using different amount of concentrated nitric acid.....	53

Figure 3.22 Raman spectra of the powder form of the films having different Co:Ti mole ratios (as marked).	54
Figure 3.23 Raman spectra recorded from the surfaces of the samples prepared with 4:7, 5:7 and 6:7 Co:Ti mole ratio.....	55
Figure 3.24 Raman spectra recorded from the surfaces of the samples prepared using different Co:Ti:C ₁₂ EO ₁₀ mole ratios.	56
Figure 3.25 SEM micrograph of the sample prepared using 4:4:1 Co:Ti:C ₁₂ EO ₁₀ mole ratio.....	57
Figure 3.26 SEM micrograph of the sample prepared using 4:4:1 Co:Ti:C ₁₂ EO ₁₀ mole ratio at magnifications a) ×200k and b) ×300k.....	58
Figure 3.27 STEM image of mesoporous CoTiO ₃	59
Figure 3.28 Elemental map of mesoporous CoTiO ₃ (upper-left: the original image, upper-right: distribution of oxygen, down-left: distribution of titanium and down-right: distribution of cobalt.) ...	60
Figure 3.29 TEM image of a mesoporous CoTiO ₃ film prepared using 4:4:1 Co:Ti:C ₁₂ EO ₁₀ mole ratio, scraped from the substrate.	61
Figure 3.30 TEM image of mesoporous CoTiO ₃ thin film prepared using 4:4:1 Co:Ti:C ₁₂ EO ₁₀ mole ratio recorded higher magnification (with ED pattern on the down-right corner).	62
Figure 3.31 TEM image of a mesoporous CoTiO ₃ monolith prepared using 7:7:1 Co:Ti:C ₁₂ EO ₁₀ mole ratio.	63
Figure 3.32 Crystalline Co ₃ O ₄ domains in mesoporous CoTiO ₃ thin film prepared using 7:7:1 Co:Ti:C ₁₂ EO ₁₀ mole ratio.....	64
Figure 3.33 XRD pattern (between 33°-40°) of the film sample containing Co ₃ O ₄ crystals in great quantities.	65
Figure 3.34. Temperature dependent XRD of mesoporous CoTiO ₃	67
Figure 3.35. Temperature dependent XRD of MnTiO ₃	68
Figure 3.36. Temperature dependent XRD patterns of mesoporous Li ₄ Ti ₅ O ₁₂	69
Figure 3.37. XRD pattern of Li ₄ Ti ₅ O ₁₂ annealed step by step up to 500 and 550 °C with phase labels	70
Figure 3.38 Temperature dependent Raman Spectra of CoTiO ₃	71
Figure 3.39 Evidence of the stoichiometric rutile formation upon phase separation in mesoporous CoTiO ₃ under the laser of the Raman spectrophotometer.....	73
Figure 3.40 Temperature dependent Raman spectra of MnTiO ₃	74
Figure 3.41 Temperature dependent Raman spectra of Li ₄ Ti ₅ O ₁₂	75
Figure 3.42 Temperature dependent isotherms of mesoporous CoTiO ₃	76
Figure 3.43 Pore size distribution plots of CoTiO ₃ at different annealing temperatures.	77
Figure 3.44 Temperature dependent isotherms of mesoporous MnTiO ₃	79

Figure 3.45 Pore size distribution plots of MnTiO_3 at different annealing temperatures.....	80
Figure 3.46 Temperature dependent isotherms of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$	80
Figure 3.47 Pore size distribution plots of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at different annealing temperatures.....	81
Figure 3.48 TEM images of mesoporous CoTiO_3 monolith (the scale bar is a) 50 and b) 20 nm).	84
Figure 3.49 TEM image of mesoporous CoTiO_3 monolith (white circles show some the mesopores).	85
Figure 3.50 TEM images of mesoporous MnTiO_3 monolith	86
Figure 3.51 TEM image of mesoporous MnTiO_3 monolith (white circles show some of the mesopores).	86
Figure 3.52 TEM images of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ monoliths	87
Figure 3.53 TEM image of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ monolith (white circles show the mesopores).....	87
Figure 3.54 TEM image of CoTiO_3 annealed step by step up to 550 °C.	88
Figure 3.55 TEM image of CoTiO_3 annealed step by step up to 550 °C (closer view).	88
Figure 3.56 N_2 sorption isotherms of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ calcined at 350 and 550 °C.	90
Figure 3.57 N_2 sorption isotherms of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared with different calcination/annealing routes.....	91
Figure 3.58 XRD patterns of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared with different calcination/annealing routes.....	92
Figure 3.59 Raman spectra of bulk CoBr_2 without any treatment, CoBr_2 calcined at 350 °C, $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ calcined at 350 °C and CoBr_2 calcined at 700 °C	94
Figure 3.60. Raman spectra recorded from the surface of the CoTiO_3 films calcined at different temperatures and prepared using CoBr_2 as Co(II) source.	95
Figure 3.61 Raman spectra recorded from the scraped powder of the CoTiO_3 films calcined at different temperatures and prepared using CoBr_2 as Co(II) source.	96
Figure 5.1 Small angle XRD patterns of as-prepared Li(I):Mn(II) samples with different salt:surfactant mole ratios	100
Figure 5.2 Raman spectra of LiMn_2O_4 samples.....	101
Figure 5.3 TEM image of a LiMn_2O_4 monolith.	102
Figure 5.4 TEM image of a single LiMn_2O_4 crystal domain	102
Figure 5.5 Raman spectrum of the LiCoO_2 thin film coated on a stainless steel substrate.....	103
Figure 5.6. LiCoO_2 material synthesized a) using MASA and b) without using surfactants	104
Figure 5.7 SEM image of LiCoO_2	104
Figure 5.8 TEM image of a single LiCoO_2 nanospherical feature (Scale bar is 2 nm).	105

Table 2.1: CoTiO ₃ samples prepared using two different Co(II) salts	27
Table 3.1: The Bragg angle and the d-spacing values of the samples prepared using different salt:C ₁₂ EO ₁₀ mole ratio.	38
Table 3.2: Temperature dependent N ₂ sorption data of mesoporous CoTiO ₃ monolithic powder.....	78
Table 3.3: Temperature dependent N ₂ sorption data of mesoporous MnTiO ₃ monolithic powder.....	82
Table 3.4: Temperature dependent N ₂ sorption data of mesoporous Li ₄ Ti ₅ O ₁₂ monolithic powder. ...	83
Table 3.5: N ₂ sorption data of mesoporous Li ₄ Ti ₅ O ₁₂ prepared with different calcination/annealing routes.....	91
Table 3.6: N ₂ sorption data of mesoporous CoTiO ₃ monolithic powders prepared using different CoBr ₂ :[Co(H ₂ O) ₆](NO ₃) ₂ mole ratios.	98

1. INTRODUCTION

In the light of recent developments in science and technology, now it has been possible to admire the touch of the nature clearer than ever. Since the very beginning of the noteworthy achievements, people got inspired from the surroundings and its harmonious perfection. As a matter of fact, while scientists built laboratories equipped with state-of-art tools, they also realized that the nature itself is an immense laboratory with its own –and mostly unachievable- technology. Therefore, nature-inspired technology forms a great deal of the nowadays daily used artificial products. For instance, an interesting aluminosilicate substance namely “zeolite”, is found in the nature with its highly porous structure which can accommodate a wide variety of cations, such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} and others due to its negatively charged framework. This particular material is nothing but a product of volcanic rocks and ash layers reacted with alkaline ground water. On the other hand, with a pore size of less than 12 Å [1], zeolites can play as a host for a high amount of water, adsorbed inside the pore channels, and they are called zeolites (“boiling rock” in Greek) for this reason. [2] Since more than a century, this “boiling rock” has been employed in many applications such as highly selective molecular sieves [3] [4], separation of different isomers and gas mixtures [5] [6], ion exchanging [7], catalysis [6] [8] and more recently cleaning up of radioactive wastes [9].

Despite being enormously advantageous in many areas mentioned above, some studies [10] showed that zeolites are not suitable for catalysis of large molecules. In fact, they are impractical in any application involving molecules larger than their pore size. However, zeolites attracted a great deal of attention over many years due to the fact that; structurally, they possess an excellent porous network. Provided with very tiny interconnected pore channels which continues along the material, their specific surface area can be higher than 750 m²/g and they are reasonably abundant to find in the nature.

1.1. Porous Materials

Considering zeolite as an introductory example, it is possible to argue that for all materials there are always some pros and cons to be taken into account. Some of the properties of the material are to be revealed and some should be suppressed in order to match with an appropriate application. As it has been briefly discussed previously, zeolite is both a good and a bad material for some purposes. Therefore, a valuable question to be asked will be: how to

tailor the ultimate porous material for the exact purpose. In order to answer that, one should be familiar enough with the concepts necessary to understand the world of porous materials and by extension -the scope of this study-, mesoporous materials.

1.2. Definition and Classification of Porous Materials

In 1994, a technical report acknowledged from the International Union of Pure and Applied Chemistry (IUPAC) titled “Recommendations for the Characterization of Porous Solids” [11] has been published. Contributed from many scientists among the world, the report contains some of the ground concepts and definitions about porous materials. According to this report; porous solids (or materials) are solids with pores, i.e. cavities, channels or interstices, which are deeper than they are wide. They are divided into three subclasses by means of their pore sizes:

- Micropores have widths smaller than 2 nm.
- Mesopores have widths between 2 and 50 nm.
- Macropores have widths larger than 50 nm.

In regards to this classification, it will be more accurate to specify the zeolites as microporous materials. One should not be in confusion with the fact that materials having nano-sized or even subnano-sized pores are sometimes called “nanoporous materials” [12]. This term is often used for materials having pores with size less than 100 nm. This statement is not totally wrong but, IUPAC notations [13] clearly states that those materials are classified as microporous, mesoporous or macroporous materials.

Some of the other helpful concepts to identify a porous material mentioned in that particular technical report are; pore volume V_p , pore size r_p , pore size distribution dV_p/dr_p (or dV/dw for cylindrical shaped pores) and specific surface area which is an extent of the surface area per 1 g of the porous material with a unit of m^2/g .

A typical microporous material will usually have a higher specific surface area in comparison to mesoporous or macroporous materials. However, in some cases, mesoporous materials might have a larger V_p and consequently, higher specific surface than some microporous materials. Therefore it is essential to notify all the parameters mentioned above while describing a porous material.

Among the three subclasses, within the scope of this study, the mesoporous materials will be covered in detail in next section.

1.3. Mesoporous Materials

Before going forward into details about how the mesoporous materials are designed and produced, it might be useful to emphasize their importance in science and technology and the benchmarks of their development.

Almost unquestionably, the mesoporous materials can meet much more demands than bulk materials due to their great ability to interact with atoms, ions, molecules and nanoparticles not only at their surfaces, but throughout the bulk of the materials. [14] The structural capabilities at nanometer scale and high surface area make the mesoporous materials very attractive in all surface-related applications such as: adsorption, separation, catalysis, sensors, drug delivery, energy storage and conversion, photonics and nanodevices, especially when dealing with large molecules. The zeolites or microporous materials are far away from meeting these demands. [15] [16] Technical advances in the fields of chemistry, materials science, biology, and engineering procured the development of the mesoporous materials with controllable structures and tunable pore architectures. In the past, a wide range of studies [17] [18] [19] [20] had been reported about mesoporous structures however, they were “invariably amorphous or paracrystalline, with pores that are irregularly spaced and broadly distributed in size” claimed by C. T. Kresge *et al.* in their published work in 1992. [21] C. T. Kresge *et al.* were the first to use the term “mesoporous molecular sieves” and to introduce the concept of liquid crystal templating to explain the mechanism for producing regularly arranged uniform pores, controlled in the range of 16 Å to 100 Å or more. This development is followed by the Japanese scientists Inagaki, Fukushima and Kuroda, who optimized the synthesis conditions and obtained a pure ordered mesoporous silicate in 1993 [22]. Since then, the soft-templating method has become a general pathway for the synthesis of ordered mesoporous materials. However, it was soon realized that this method was insufficient to prepare many non-siliceous mesostructured materials. After the realization of this obstacle, a new method has been developed by R. Ryoo *et al.*, called “hard templating”, from which they successfully synthesized highly ordered mesoporous carbon. [23] Since then, hard templating has been employed to produce many non-siliceous mesoporous metal oxides. [24] [25] Recently, some soft-templating methods have also been developed to produce non-siliceous mesoporous metal-oxide materials. [24]

1.4. Soft-Templating for Non-Siliceous Mesostructures

In general, soft-templating refers to a production method of mesoporous materials using soft chemistry. It involves a liquid crystalline (LC) phase made with surfactant molecules and inorganic species locked up in between micellar domains of the LC phase. Typically, it requires: a preparation of a clear solution of the previously mentioned ingredients, a gelation step, where the self-assembly takes place and removal of the surfactant leaving behind a residue, which is actually the mesoporous material. Putting it like this makes the procedure seems very easy however, the diverse condensation/crystallization behaviors of the inorganic species and the complexity of the surfactant micelle-inorganic precursor interaction makes the process surprisingly complicated. In this sense, the chemistry of only few materials has been so far extensively understood. The first engineered materials in the mesoporous world are silicates, due to their easy, controllable, and well established chemistry.

The tetra-connected covalent bonds of silicates allow facile synthesis routes and the product material is in a flexible amorphous stable phase. However, the synthesis of non-siliceous mesoporous metal oxides is considered to be much more complex due to their susceptibility to hydrolysis condensation, redox reaction and rapid crystallization accompanied by a structural collapse. [24] Since the discovery of soft-templating for producing mesoporous silicates, many efforts have been put to find new synthetic ways for non-siliceous mesoporous materials.

For instance, the so-called evaporation induced self-assembly (EISA) process, initially proposed by Brinker and colleagues, [26] offered a new, easy and fast way to produce siliceous and non-siliceous binary and mixed metal oxides compared to the hard templating methods. In their pioneering work, they suggested that the initial solution is dilute enough to have surfactant concentration way below the critical micelle concentration (cmc). Due to the low viscosity of the starting solution, coating can be applied in many ways. A substrate is dipped into the solution and a mesophase is formed upon the evaporation of the volatile solvent. Because the concentration of the surfactant reaches well above the cmc near the surface of the film, a liquid crystalline phase nucleates and a solidified network is formed. The solidification is due to condensation of the metal organic species and the self-assembly of the inorganic network is done via the interactions between the charged head group of the ionic surfactant and the metal oxy/hydroxy sites of the inorganic species. This technique works well for silica, alumina and titania materials. However, the slow condensation dynamics of

different metal organic precursors make the system not beneficial for the entire binary and ternary metal oxides. Because the state/phase of the metal salts in the LLC phase is not known, the method does not give a full insight about the metal salt-surfactant mesophases. On the other hand, some examples of mesoporous non-siliceous metal oxide synthesis have been reported using EISA approach.

Antonelli *et al.* have synthesized mesoporous transition metal oxides by a ligand-assisted templating method. A new mesoporous niobium oxide doped with vanadium (V) was obtained, [27] where the ligand bonded to the metal sites reduced the hydrolysis and controlled this process to prevent bulk formation.

Sanchez *et al.* systematically investigated the formation mechanism of EISA and synthesis parameters of poly(ethylene oxide) (PEO) type surfactants templated mesoporous materials. Mesoporous transition metal (Y–Zr, Ti, Zr, V, Fe, etc.) oxide-based hybrid thin films have been prepared reproducibly with variable structures. [28] [29] There are many successful examples in the literature that employed the EISA method however; the products have usually large pores due to long PEO copolymer used in templating.

The preparation of different mesoporous metal oxides relies on understanding the nature of the precursors and optimizing each of the parameters listed below: [30]

- i) Inorganic hydrolysis and condensation have to be mastered, to avoid the instantaneous formation of an inorganic network, which would irreversibly a poorly organized structure,
- ii) The metal salt concentration should be carefully set to an optimum value,
- iii) The surfactant type should be chosen properly and the attractive force between inorganic species and the surfactant should be well understood in order to orchestrate an assembly process,
- iv) A non-aqueous volatile solvent should be used in order to accelerate the solvent evaporation.

The major drawback in the EISA synthesis is that the inorganic precursor/surfactant ratio is very low, in other words, loading of the metal ions to form mixed oxides is very limited. Besides, large poly(ethylene oxide) used for mesostructuring non-siliceous oxides result in a structure with large pores and thick pore walls.

1.5. Molten Salt Assisted Self Assembly (MASA) Synthesis of Mesoporous Metal Titanate Thin Films

In 2011, Dag *et al.* reported a study on the principles of the formation and stability of a hydrous metal nitrate- $C_{12}EO_{10}$ ($C_{12}EO_{10}$ is 10-lauryl ether) mesophase. They focused on $[Zn(H_2O)_6](NO_3)_2$ and $[Cd(H_2O)_4](NO_3)_2$ as the inorganic precursors and demonstrated that the metal salt acts as a solvent by staying in the molten phase due to the soft confinement effect (SCE) in the small hydrophilic domains of the mesophase. They also found out that other metal nitrate salts can also form a mesophase with $C_{12}EO_{10}$ and collaborative assembly of $C_{12}EO_{10}$ with CTAB, an ionic surfactant is needed in order increase the salt to surfactant ratio. [31] Following this, they soon realized that a synthetic pathway with the removal of the surfactant from the salt-surfactant mesophase by calcination, can be used for the synthesis of mesoporous metal oxide coated-silica. Those films can be converted into metal chalcogenite nanoflake thin films in two steps by exposing the films into H_2E (E is S and Se) and then dilute HF solution. [32] Recently, the same group extended their studies for the synthesis of metal chalcogenide-titania systems by switching the polymerizing agent from silica source to a titania source (titanium(IV)butoxide) by optimizing the synthesis conditions. [33] In their published work, they first introduced the so called molten salt assisted self-assembly (MASA) synthesis as a universal method for siliceous and non-siliceous mesoporous metal oxides.

The beauty of MASA comes from its versatility, producing many different mesoporous thin films with high surface area and uniform pore size via a molecular assembly process, which could not be achieved using former techniques. The molten salt, locked in small domains, acts as secondary solvent (the first one is ethanol or water) and helps to organize surfactant molecules into mesophase. The use of charged surfactant (CTAB) in addition to the non-ionic surfactant ($C_{12}EO_{10}$) provides charge stabilization to the metal species in the hydrophilic domains of the mesophase and hence, increases the loadable amount of the metal ion into the mesophase, up to 8:1 metal ion to surfactant mole ratio. [34] In the MASA synthesis of metal titanates, titanium(IV)butoxide is used for 3-D network formation (hydrolysis/condensation), which is slowed by the addition of nitric acid (HNO_3) to create highly acidic medium. Under these conditions, the condensation is hindered by protonation of the M-OH nucleophilic species present in the medium.

Listed below are the important points in MASA synthesis of mesoporous metal titanates:

- i. different from other methods, two solvents are used in MASA synthesis. One is ethanol, a volatile solvent necessary to homogenize the mixture of the ingredients and the second one is the molten salt, which involves in the formation of the mesophase and constitutes the metal ion source of the targeted metal titanate,
- ii. titanium(IV)butoxide, a reagent very prone to hydrolysis in the existence of water, is the polymerizing/networking agent as well as the Ti(IV) source. A strong acidic medium is necessary to slow its hydrolysis,
- iii. the use of an ionic surfactant (CTAB) allows high loading of the metal salt by neutralizing the interfacial charges between the salt species and surfactants domains,
- iv. the clear solution including all ingredients (metal and titania sources, surfactants, ethanol and acid) is a liquid with low viscosity, making it useful in all coating processes. Spin and spray coating can be employed to any desired substrate (glass, quartz, Si wafer, Al foil, *etc.*),
- v. the calcination temperature range lies between 350 to 600 °C and the synthesis is convenient for fast calcination (10-30 min),
- vi. the product obtained via spin coating is usually a mesoporous thin film, displaying optical transparency. Spray coating is chosen in the situation when large amount of material is required and the product is a monolithic powder, which can easily be scraped from the substrate.

1.6. Metal-Titanates

Metal titanates with the general formula of MTO_3 are usually wide band gap semiconductors and of great interest in many fields. They have wide applications for industries, such as semiconductor rectifiers, electrodes of solid oxide fuel cell, metal–air barriers, color mixtures of surface coating, gas and humidity sensing devices [35], and dye-sensitized solar cells. [36] The MTO_3 family of metal titanates often crystallizes in two structures. The first one is the perovskite type structure (e.g. SrTiO_3) and the second one is ilmenite type structure (e.g. FeTiO_3 , NiTiO_3 , CoTiO_3 ...etc.) [37]

Other interesting members of metal titanate family are the alkaline and alkaline earth metal titanates such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Na}_2\text{Ti}_6\text{O}_{13}$, MgTiO_3 , BaTiO_3 , SrTiO_3 , etc. These materials have photoelectric, ferroelectric, piezoelectric, and dielectric properties and are used in lithium ion intercalation, photocatalysis of organics and water splitting processes. For instance, SrTiO_3 is

a well-known photocatalyst for the decomposition of some organic compounds and production of hydrogen by water splitting under UV light irradiation. [38]

1.6.1. Literature on CoTiO₃

Among metal titanates, CoTiO₃ belongs to the ilmenite type structure family (like FeTiO₃). It is an antiferromagnetic semiconductor material with Néel temperature of approximately 38 K [39] and a direct band gap of 2.53 eV. [40] It has high-k dielectric properties making it a strong candidate for replacing SiO₂ gates in CMOS technology. [37] Otherwise, CoTiO₃ is used in applications such as humidity [41] and gas sensors. [42] Chu *et al.* showed that CoTiO₃ nanopowder with increased surface area is good material for ethanol sensing application. [43] Sarkar *et al.* synthesized a CoTiO₃/TiO₂ heterostructure used in oxidative dehydrogenation of cyclohexane with good conversion efficiencies and benzene selectivity. [44]

In the literature, many works on different CoTiO₃ materials have been published. For instance, Cheng-Gao Sun *et al.* reported a mesoporous Co-Ti oxide material with specific surface area of 204 m²/g. [45] However, the product was in the powder form and the phase of the material was also not clearly identified. They mentioned about a mixture of Co dispersed in anatase TiO₂ and unidentified Co-O-Ti compound. Guorui Yang *et al.* reported an interesting material such as CoTiO₃ nanofibers with specific surface area of 20 m²/g. [46] A.V. Vinogradov *et al.* succeeded to synthesize crystalline CoTiO₃ coatings at low temperatures; however, no mesoporous features have been reported. [47] B. C. Yadav *et al.* reported a nanostructured CoTiO₃ film for humidity sensing application with an average crystal size of 21.5 nm and, still no surface area results have been reported. [48]

1.6.2. Literature on MnTiO₃

Similar to CoTiO₃, MnTiO₃ is an antiferromagnetic semiconductor material with ilmenite structure. [49] [50] Recently, MnTiO₃ has attracted much attention for its strong absorption in the visible region which may be suitable to the utilization of solar energy. [51] In a conventional Grätzel cell or dye sensitized solar cell (DSSC) [52], TiO₂, as a wide band gap semiconductor, is sensitized with dye molecules in order to capture the photo-generated electrons. Enhessari *et al.* and Seong *et al.* have recently reported that the DSSCs designed with MnTiO₃ coated TiO₂ had improved energy conversion efficiency. [53] [54] He *et al.*

showed that MnTiO_3 displays electrical resistance variation in the existence of humidity, thus making MnTiO_3 a candidate for humidity sensing applications. [55]

So far in the literature, there exist only few works about nanostructured MnTiO_3 . M. Enhessari *et al.* and G. Zhou *et al.* reported MnTiO_3 nanoparticles with sizes 22 -30 nm and 50 nm, respectively. [56] [57] [58] There exists in the literature other manganese based mesoporous materials, typically manganese oxides/ TiO_2 heterostructures, with fair BET surface area [59] [60] [61] [62] [63], yet, not higher than the results of this study, which will be shared later in section 3.4.3.

1.6.3. Literature on $\text{Li}_4\text{Ti}_5\text{O}_{12}$

Beyond any doubt, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is the most highlighted material among the three metal titanates presented in this work. Owing to its Li^+ intercalation capability, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is being widely used as an anode material in Li-ion batteries. The defect spinel structure of the material allows the material to transform to $\text{Li}_7\text{Ti}_5\text{O}_{12}$ (a lithiated phase) with a negligible volume change during charging/discharging. [64] Countless work published in highly-ranked journals has been carried out to enhance the charge/discharge capability, cycle lifetime and the surface area of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by matching it with other conductive, phase stabilizing and mesoporous materials (e.g. composites with carbon nanotubes, graphene sheets). These attempts will not be discussed here because it is beyond the scope of this study. However, some studies about the production and characterization of nanostructured pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are worth to mention.

Liu *et al.* [65] synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles using a hydrothermal method. They measured a BET surface area of $37 \text{ m}^2/\text{g}$ and a pore size of 6-8 nm. Kim *et al.* [66] reported mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ microspheres displaying a BET surface area of $69 \text{ m}^2/\text{g}$. Another microsphere feature was reported by Nugroho *et al.* [67]. They introduced a facile template-free production method to produce hierarchical mesoporous microspheres which exhibited a BET surface of $117 \text{ m}^2/\text{g}$ and a mean pore size around 2-10 nm. Recently, Sun *et al.* [68] followed a direct-synthesis-from-solution method to produce mesoporous nanoclusters with high BET surface area of $142 \text{ m}^2/\text{g}$ and small pore sizes (2-6 nm). Chen *et al.* [69] succeeded to produce interesting 2-D “saw tooth-like” nanosheets. The structure did not display typical mesoporous behaviour however, due to the high aspect ratio of nanosheets; the material exhibited a high BET surface area of $139 \text{ m}^2/\text{g}$. The pore size is undefined because the 2-D nanosheets displayed a different structure than the porous materials defined in the IUPAC

standards. Another interesting $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanosheet was recently reported by Sha *et al.* and the material displayed a very high BET surface area of $174 \text{ m}^2/\text{g}$.

Notice that all these synthesized materials mentioned above are powders and no method for thin film production of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been proposed yet. MASA seems to be a powerful method to fulfil this requirement.

2. EXPERIMENTAL PROCEDURE

2.1. The General Route for Sample Preparation

An initial solution containing 2 different surfactants ($C_{12}H_{25}(OCH_2CH_2)_{10}OH$, $C_{12}EO_{10}$, and $C_{16}H_{33}N(CH_3)_3Br$, CTAB), nitrate salt ($[Co(H_2O)_6](NO_3)_2$ or $[Mn(H_2O)_6](NO_3)_2$ or $LiNO_3$) of the convenient metal, titanium(IV)butoxide ($Ti(OC_4H_9)_4$) as titania source and ethanol as solvent is prepared at an appropriate pH. Spin coating is employed to coat the substrates with this solution. The synthesis is completed with a fast calcination step (10-20 min) at temperatures ranging between 350 °C and 550 °C in air atmosphere. Further annealing at higher temperatures is done in air atmosphere as well, if necessary. The general route for sample preparation is depicted in **Figure 2.1**.

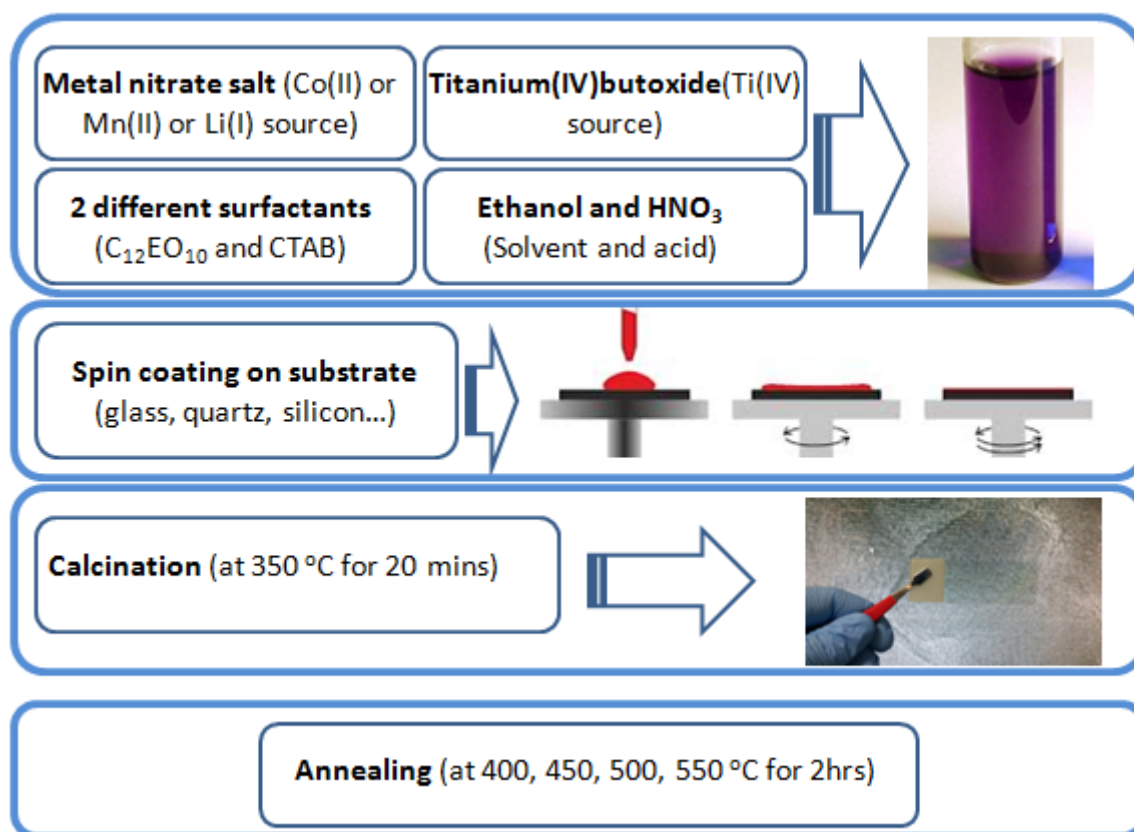


Figure 2.1 The general route for sample preparation

2.2. General Optimizations

2.2.1. Optimizations of the Amount of Concentrated Nitric Acid

2.2.1.1. *As-Prepared Films*

The optimization for the amount of the concentrated nitric acid (HNO_3) has been done for CoTiO_3 samples. For this purpose, the general route for sample preparation has been followed except from last calcinations part, in order to maintain the sample in the liquid crystalline phase. The solutions are spin coated at 1500 rpm. A constant mole number of $n = 0.8$ mmol has been set to make calculation and notation easier. 10 samples containing a constant 5.6 mmol $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$, 5.6 mmol $(\text{Ti}(\text{OC}_4\text{H}_9)_4)$, 0.8 mmol CTAB, 0.8 mmol 10-lauryl ether ($\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$, abbreviated as $\text{C}_{12}\text{EO}_{10}$) and 7 g of pure ethanol but different amounts of conc. HNO_3 : 650 mg, 600 mg, 550 mg, 500 mg, 450 mg, 400 mg, 350 mg, 300 mg, 250 mg, 200 mg, 150 mg, 100 mg, 25 mg and 0 mg, respectively, are prepared. The x-ray diffraction (XRD) patterns were obtained and the optical microscope images have been taken.

2.2.1.2. *Calcined Films*

The general route for sample preparation has been followed in order to prepare 2 spray coated samples from a solution of 3.2 mmol $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$, 3.2 mmol $(\text{Ti}(\text{OC}_4\text{H}_9)_4)$, 0.8 mmol CTAB, 0.8 mmol $\text{C}_{12}\text{EO}_{10}$ and 7 g of pure ethanol. The first sample was prepared by using 50 mg of conc. HNO_3 and the second sample by 500 mg. Then these samples were calcined using the same parameters (calcination temperature and period). Powders were collected by scraping many substrates in order to obtain enough samples for N_2 sorption measurement. Brunauer-Emmett-Teller (BET) surface area calculations were used for specific surface area determination and Barrett-Joyner-Halenda (BJH) calculations from the desorption isotherms were used for plotting the pore size distribution and determining the average pore size.

2.2.2. Optimization of the Metal to Surfactant Ratio

The optimization for the metal salt:titanium source:surfactant ratio has been done for CoTiO_3 samples. The general route for sample preparation has been followed in order to prepare 6 samples with different Co:Ti: $\text{C}_{12}\text{EO}_{10}$ ratios. The titanium(IV)butoxide, CTAB, $\text{C}_{12}\text{EO}_{10}$, ethanol and conc. HNO_3 kept constant at 5.6, 0.8, 0.8 mmoles, 7, and 0.5 g, respectively. The

amount of $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ were increase from 0.8 to 4.8 mmols step by step. XRD patterns of the as-prepared samples and the Raman and UV-vis absorption spectra of the calcined samples were collected.

2.2.3. Optimization of the Calcination Temperature

The optimization for the calcination temperature has been done for the CoTiO_3 sample prepared via the general route described above and by spin coating the clear solutions at 1500 rpm over glass slides. The sample was first calcined at 140 °C for 20 minutes and annealed at 160, 180, 200, 210, 220, 230, 240, and 300 °C for 20 minutes at each temperature. At each step, a Raman spectrum has been collected in order pursuit the oxide formation.

2.2.4. Optimization of the Calcination Time

Two identical cobalt containing as-prepared film samples have been prepared. The first sample has been calcined at 350 °C for 20 minutes and the second sample has been subjected to a longer calcinations route. Starting from 25 °C, the film has been heated to 350 °C with a ramp of 1 °C/min and left at 350 °C for 2 hrs. The calcinations of the second sample took approximately 7 hrs and 25 minutes. Raman spectra of both films have been collected.

2.3. Preparation of Powder CoTiO_3

In order to prepare large amount of monolithic CoTiO_3 powder, the general route for sample preparation with spray coating method has been employed. 4n:4n:n ($\text{Co}:\text{Ti}:\text{C}_{12}\text{EO}_{10}$) molar ratio has been chosen for the composition. The initial calcinations temperature is set to 350 °C. 135 mg of monolithic CoTiO_3 powder was obtained by scraping 12 glass substrates. This powder is then subjected to annealing procedure at 400, 450, 500 and 550 °C for 2 hrs. XRD patterns, Raman spectra and N_2 sorption isotherms have been collected for the initial calcination step and each annealing step consecutively.

2.4. Preparation of Powder MnTiO_3

The same sample preparation, calcination, annealing and characterization procedures with the same compositional ratio of 4n:4n:n as CoTiO_3 , have been followed for MnTiO_3 as well.

2.5. Preparation of Powder $\text{Li}_4\text{Ti}_5\text{O}_{12}$

Almost the same sample preparation, calcination, annealing and characterization procedures have been followed for $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The slight differences are; the compositional ratio was set to 4n:5n:n Li(I):Ti(IV): $\text{C}_{12}\text{EO}_{10}$ in order to maintain the stoichiometric ratio between Li and Ti and the calcination time has been prolonged to 1.5 hrs in order to totally get rid of the unburned surfactants (which was not the case for CoTiO_3 and MnTiO_3).

2.6. CoTiO_3 prepared using CoBr_2 as a cobalt source

2.6.1. Preparation of the samples and N_2 sorption measurements

The general route for the sample preparation was followed in order to prepare 5 monolithic powder samples with different ratios of CoBr_2 to $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$. The samples were calcined at 350 °C and 12 substrates were scraped in order to collect more than 100 mg of monolithic powder from each composition. The sample names with their composition are given in the **Table 2.1**.

Table 2.1: CoTiO_3 samples prepared using two different Co(II) salts

	CoBr_2	$[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$	Co to Ti to $\text{C}_{12}\text{EO}_{10}$ ratio
CT4A	0 %	100 %	4n:4n:n
CT4AB1	25 %	75 %	4n:4n:n
CT4AB2	50 %	50 %	4n:4n:n
CT4AB3	75 %	25 %	4n:4n:n
CT4B	100 %	0 %	4n:4n:n

2.6.2. Raman Spectroscopy

The general route of sample preparation was followed in order to prepare a spin coated thin film sample with the composition same as CT4B. Raman spectra were collected both from the surface of the film and the scraped powder from the same film.

2.7. Sample preparation for TEM imaging

All the samples prepared for TEM imaging were initially prepared according to the general route of sample preparation. The spin speed of the spin coater has been set to 7000 rpm in order to obtain the thinnest film possible. The calcination route differed slightly from sample to sample. The film is scraped from the surface of the substrate with the help of another clean glass substrate. The half of the powder constituting of monolithic film pieces is put into a vial containing pure ethanol. The other half of the powder is grinded in an agate mortar for 15 minutes. The grinded powder is also added into the same ethanol containing vial and the mixture is sonicated for 30 minutes, allowing the particles to disperse. A carbon coated Cu grid with 300 mesh placed on a clean paper towel. A powerful lamp is placed on top of the paper towel in order to shine light where the grid is located. 3-5 drops of the dispersed mixture is dropped on the grid and the grid is let drying under the above light for 10 minutes.

2.8. Chemicals and Instrumentation

All chemicals were purchased from Sigma Aldrich. The micro-Raman spectra were recorded on a LabRam confocal Raman microscope with a 300 mm focal length. The spectrometer was equipped with a Ventus LP 532, 50 mW, diode pumped solid-state laser operated at 20 mW, with a polarization ratio of 100:1, a wavelength of 532.1 nm, and a 1024x256 element CCD camera. The signal collected was transmitted via a fiber optic cable into a spectrometer with 600 g/mm grating. The Raman spectra were collected by manually placing the probe tip on the desired point of the sample over the glass or silicon wafer. The UV-vis absorption spectra were recorded on Carry 5 UV-Vis spectrophotometer using thin films, coated over quartz substrates. The XRD patterns were recorded on a Rigaku Miniflex diffractometer using a high power Cu-K α source operating at 30kV/15mA. The OM images were obtained in transmittance mode on a ZEISS Axio Scope A1 polarizing optical microscope. The SEM images were recorded using Hitachi HD-2000 STEM in SEM mode and ZEISS EVO 40. The high resolution transmittance electron microscope (HRTEM) images were recorded on a JEOL JEM 2100F at an operating voltage of 200 kV. The N₂ (77.4 K) sorption measurements were performed with a TriStar 3000 automated gas adsorption analyzer (Micrometrics) in a relative pressure range, P/P_0 , from 0.01 to 0.99. GISAXS measurement was performed with NANO VIEWER (Rigaku) equipped with Micro Max-007HF high intensity micro focus rotating anode X-ray generator during 10 mins.

3. RESULTS & DISCUSSION

3.1. The Effect of acid on the mesophase and mesoporous CoTiO_3 thin films

In general, the titanium alkoxides hydrolyze rapidly and condense in water into amorphous titanium oxy hydroxy species. [70] [28] In MASA process, this quick polymerization of titanium alkoxide is hindered by the addition of acid. As a consequence, metal-titania interaction is enhanced in order to form the metal titanates. The more dispersed the titania domains are, the more efficient Ti-O-M bond will form and a more ordered mesostructure will be obtained. In other words, adding acid into the solution slows down the polymerization of titania domains by suppressing the $[\text{OH}]^-$ population and creates more active site for guest metal to form bond.

Small angle XRD is a powerful tool to determine the liquid crystalline order and by extension, the order of the mesostructure. **Figure 3.1** and **Figure 3.2** show the small angle XRD patterns of as-prepared samples with different amounts of acid.

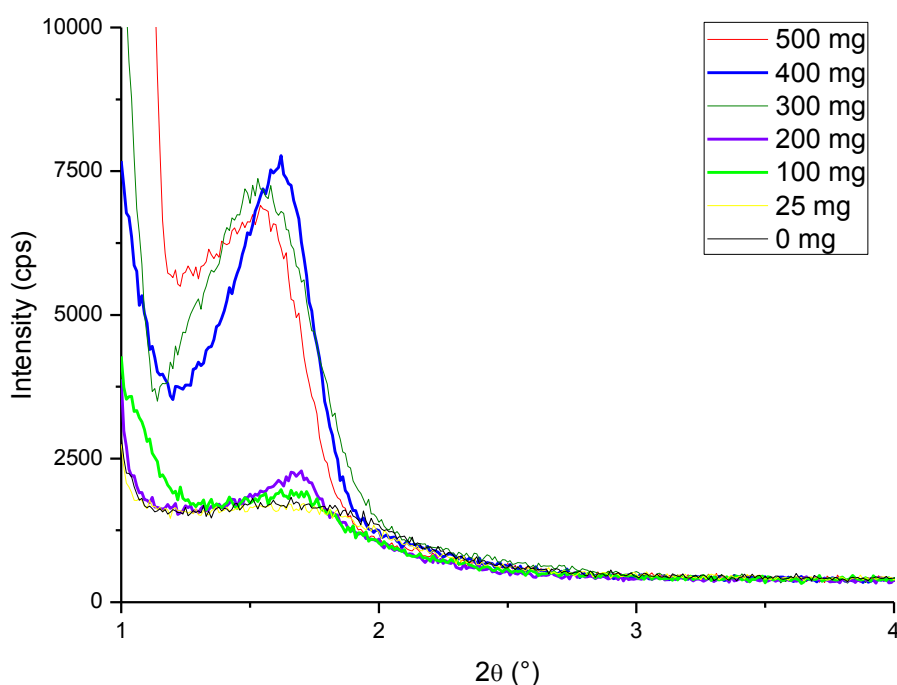


Figure 3.1 The XRD patterns of the as-prepared samples with different amount of acid (as marked in the patterns with a colour code), low amounts.

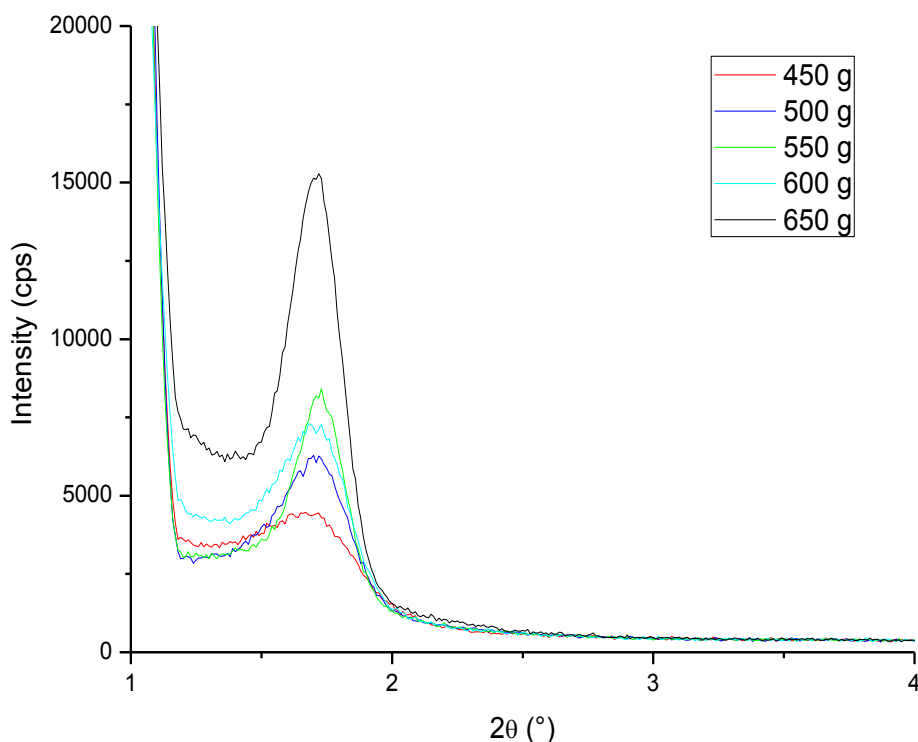


Figure 3.2. The XRD patterns of the as-prepared samples with different amount of acid (as marked in the patterns with a colour code), high amounts.

Figure 3.1 clearly shows that, there is a relation between the amount of acid and the meso-order. Furthermore, there is also a breaking point after 200 mg of acid and starting from 300 mg, the as-prepared film gets more and more ordered compared to the lower ones. Even though, the intensity of XRD lines can be misleading the meso-order, if the measurement is supported by measuring many samples and if they are all held in the same conditions, the peak intensity can be utilized for meso-order comparison. In this case, all the films were produced in the same way and they all have similar thickness. Therefore, it is reasonable to say that there is a sharp transition between the samples prepared using 200 mg and 300 mg of acid. The changes in the XRD patterns of the samples prepared using higher amounts are not as clear (compare **Figure 3.1** and **Figure 3.2**). Similarly, the optical microscopy (OM) images display drastic changes by increasing the amount of acid from 200 to 300 mg. The image of the sample prepared using 200 mg of acid displays worm-like features, but that of the sample, prepared using 300 mg of acid shows a continuous smooth surface morphology (compare images in **Figure 3.3**).

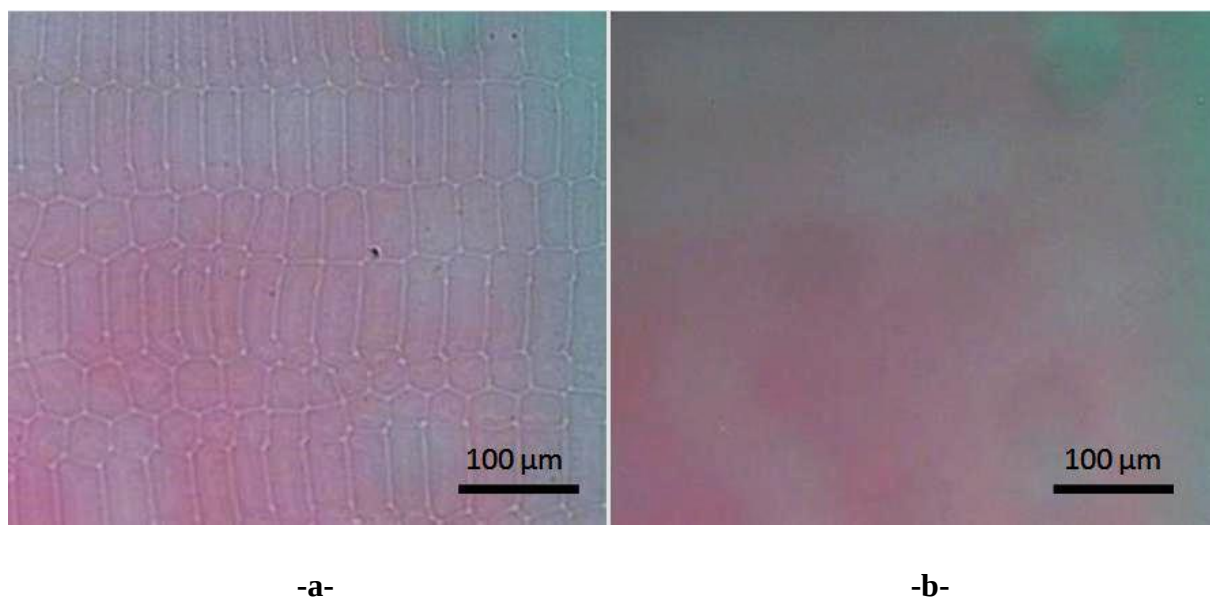


Figure 3.3 OM image of **a)** a sample containing less than 200 mg of acid and **b)** more than 300 mg of acid

However, backing up the primary hypothesis, the mesostructure exhibits the same trend upon increasing acid even further and the general trend after 200 mg of acid and higher remains constant. So there is a strong relationship between the amount of acid and the meso-order. The XRD results are supported by the OM images of the as-prepared samples; it has been clearly shown that increasing the amount of acid in the initial solution leads to a more ordered mesophase in the liquid crystalline phase. An initial more ordered mesophase is a good groundwork for the calcination step, the process where the actual mesoporous metal titanate solid network is formed. In other words, homogeneously distributed surfactant domains surrounded by homogeneously distributed molten metal salt and titania species, polymerized in reasonably small size, is an ideal place to start to construct a mesoporous structure with high specific surface area and more importantly, homogeneous pore size distribution. In order to verify this, N_2 sorption measurements have been done for two samples prepared using 50 and 500 mg of acid. The full isotherms and pore size distribution plots are shown in **Figure 3.4** and **Figure 3.5**.

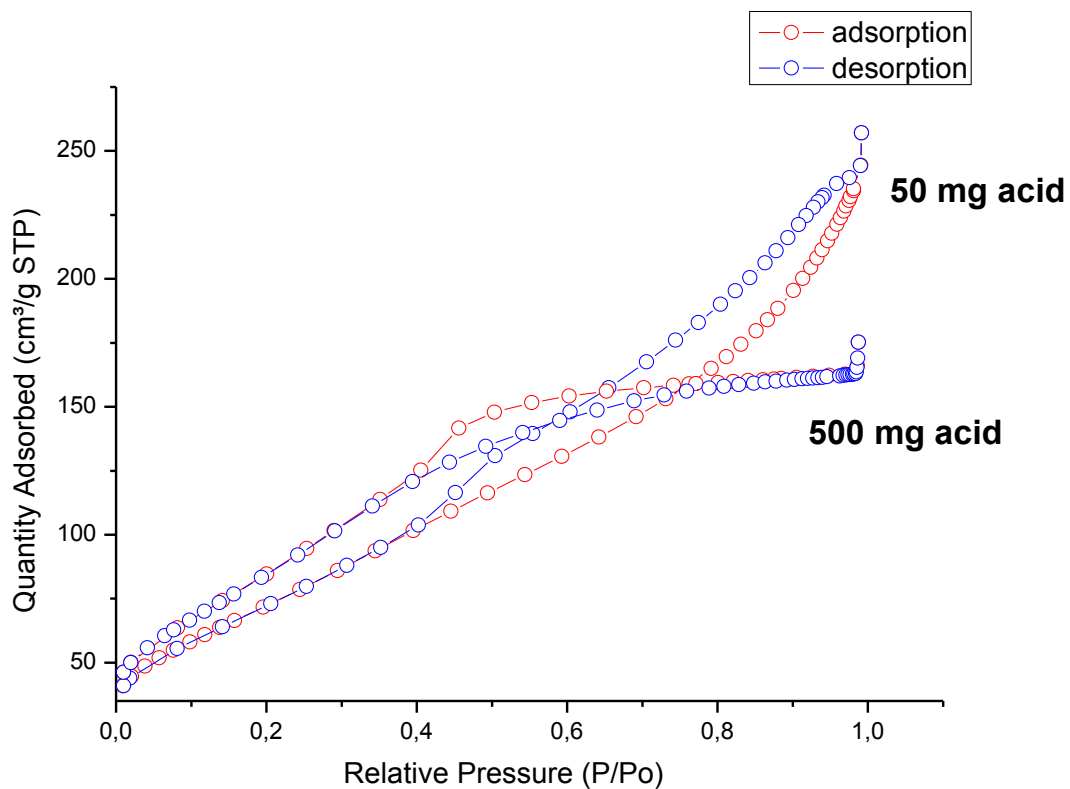


Figure 3.4 N_2 (77.4 K) sorption isotherms of both samples prepared using 50 mg and 500 mg of concentrated HNO_3 .

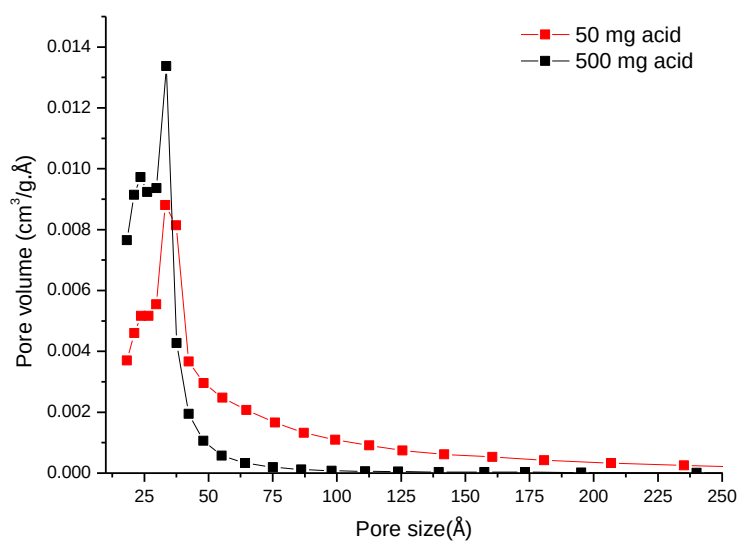


Figure 3.5 The pore size distribution of both samples prepared using 50 mg and 500 mg of concentrated HNO_3 .

Both samples, prepared using 500 and 50 mg of concentrated HNO_3 , display type IV isotherms. The difference in the slopes of the first five adsorption points suggests that the surface area is different for the two samples. Calculated BET surface areas for the samples prepared using 500 mg and 50 mg are 318 and 266 m^2/g , respectively. Considering the % error in N_2 sorption measurements, as $\pm 10\%$, the difference between two BET values is not very significant. The reason to this small decrease might be the nonporous bulk crystallization of Co_3O_4 domains which contribute to the mass but, not to the surface area. On the other hand, the decrease in the amount of acid in the initial solution seems to widen the peak in the pore size distribution plot of the final material. It is most likely because of the initially formed and poorly oriented titania domains, caused by low acidic medium. The hysteresis of the sample prepared using 50 mg extends towards region III, the macroporous region. This is also probably caused by the worm-like features observed in the OM images. However, the hysteresis in the two samples have a common endpoint (both around $P/P_0 = 0.4$) in their isotherms and a small shoulder in the micropore region in their pore size distribution plots. This behavior shows that these two materials have similar pore systems in the micropore and mesopore scale. Therefore, each of the worm-like structures has probably identical properties to those, which are in the form of thin film.

The specific pore volume of the sample prepared using 50 mg of acid is interestingly much higher than the sample prepared using 500 mg of acid (0.40 and 0.26 cm^3/g , respectively). This increase in the pore volume is due to the worm-like structure related macropores. From this point of view, worm-like features might be undesired due to the salt leaching and bulk crystallization however; it would be a wise decision to produce salt-less, pure titania in the worm-like structure. That hypothetical material might display all three pore systems, large pore volume and excellent surface area.

However, within the scope of this study, which is producing mesoporous metal titanate thin film with pure phases, high surface area, controlled and homogeneous pore size and enhanced pore wall crystallinity; the worm-like structure in the materials has been avoided because it had a negative effect on almost all the as-mentioned parameters.

Despite all the encouraging facts that are concluded from XRD and BET studies about how the acid increases the liquid crystalline order and by extension, the surface area, and the homogeneity of the pore size of the metal titanates; adding more acid than 500 mg brings other disadvantages. As already mentioned before, titanium(IV)butoxide polymerizes in the presence of water. Increasing the acid up to a certain point hinders this polymerization and the

formation of oxo-bridges. However, the concentrated nitric acid contains 68% HNO_3 and still, 32 % water. It means, when acid is added, a proportion of water is automatically introduced into the solution as well. This proportion of water is avoidable at low amounts but, it becomes dominant at very high acid concentration and influences the hydrolysis and condensation processes of titania species. Even though the ordered mesophase is still preserved, some of the active Ti-O- sites are closed to Co(II) ions. As a consequence, the yield of the Co-O-Ti bond formation is hindered, leading to the formation of separate oxides such as Co_3O_4 and TiO_2 . This situation does not cause to a formation of totally separated oxides however, it decrease the amount of synthesized CoTiO_3 by increasing the Co_3O_4 and TiO_2 formation. In order to verify this, UV-visible absorption spectra of samples with different amount of acid have been collected. The spectra of 3 mesoporous CoTiO_3 thin films prepared with 500, 600, 700 mg of acid have been compared in **Figure 3.6**.

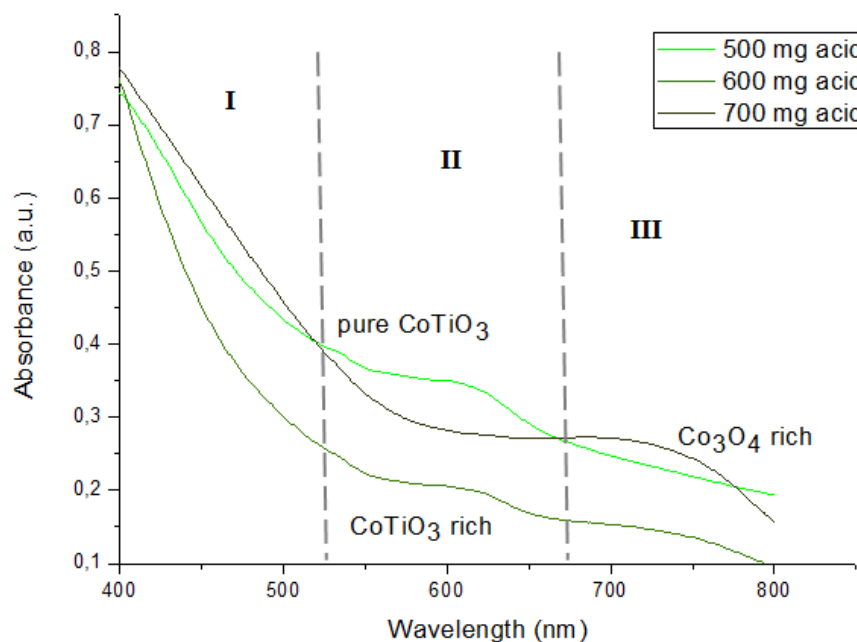


Figure 3.6 The UV-visible spectra of mesoporous CoTiO_3 thin films prepared using (a) 500, (b) 600, and (c) 700 mg of concentrated HNO_3 .

The UV-visible absorption spectra of the samples prepared using 500 and 700 mg of acid have definite difference in terms of their absorption spectra. The spectrum is divided into three regions for a better visualization. The absorption edge in region-I corresponds to the absorption of CoTiO_3 , which has a band gap of 2.53 eV. [40] The broad peak in the region-II represents the absorption of the Co(II) ions in an octahedral crystal field similar in the oxide matrix. The second peak in the region-III is the absorption of Co_3O_4 which is a material with

optical band gap of 1.52 eV [71]. In its natural form, CoTiO_3 is a green material. Normally, a material with optical band gap of 2.53 eV should be yellowish however, in the CoTiO_3 case, the existence of Co(II) ions in an octahedral crystal field creates another absorption band around 610 nm (red region of the electromagnetic wave). The combination of these two absorptions gives CoTiO_3 its natural green color and the presence of the absorption around 610 nm is considered as a clear evidence of CoTiO_3 formation. In this regard, sample prepared using 500 mg of acid is considered to be pure or nearly pure CoTiO_3 . On the other hand, the sample prepared using 700 mg of acid has another absorption in region-III, apart from the natural absorption of CoTiO_3 , which is in the boundaries of region-I. This indicates that, apart from the readily formed CoTiO_3 , there is also some Co_3O_4 in the structure. The sample prepared using 600 mg of acid exhibits an optical property somewhere between the samples prepared using 500 and 700 mg of acid due to its relatively low absorption in region-II compared to the sample which is considered as pure CoTiO_3 and in region-III compared to the sample which is considered as Co_3O_4 containing CoTiO_3 . From these implications, it is not incorrect to claim that the amount of acid added above 500 mg, triggers the formation of Co_3O_4 by restraining the titanium(IV) butoxide to react with Co(II) in the initial mesophase.

Figure 3.7 shows the SEM micrographs of two samples prepared using 500 and 800 mg of concentrated nitric acid, respectively. The sample shown in **Figure 3.7a** exhibits good homogeneity throughout the film and no crystal domains can be discerned from the general film. On the other hand, in the micrograph of the sample prepared using 800 mg of acid (**Figure 3.7b**) some noticeable white spots creates contrast in the image. The size of these spots is no more than 30 nm in diameter (undetectable with OM) and their distribution in the image is curiously homogenous. These white spot might possibly be the Co_3O_4 nanocrystals formed on top the mesoporous CoTiO_3 thin film. Figure 3.7c and 3.7d are the micrographs of the same samples in the Figure 3.7a and 3.7b, respectively, taken at higher magnifications. The Co_3O_4 nanocrystals are circled in red.

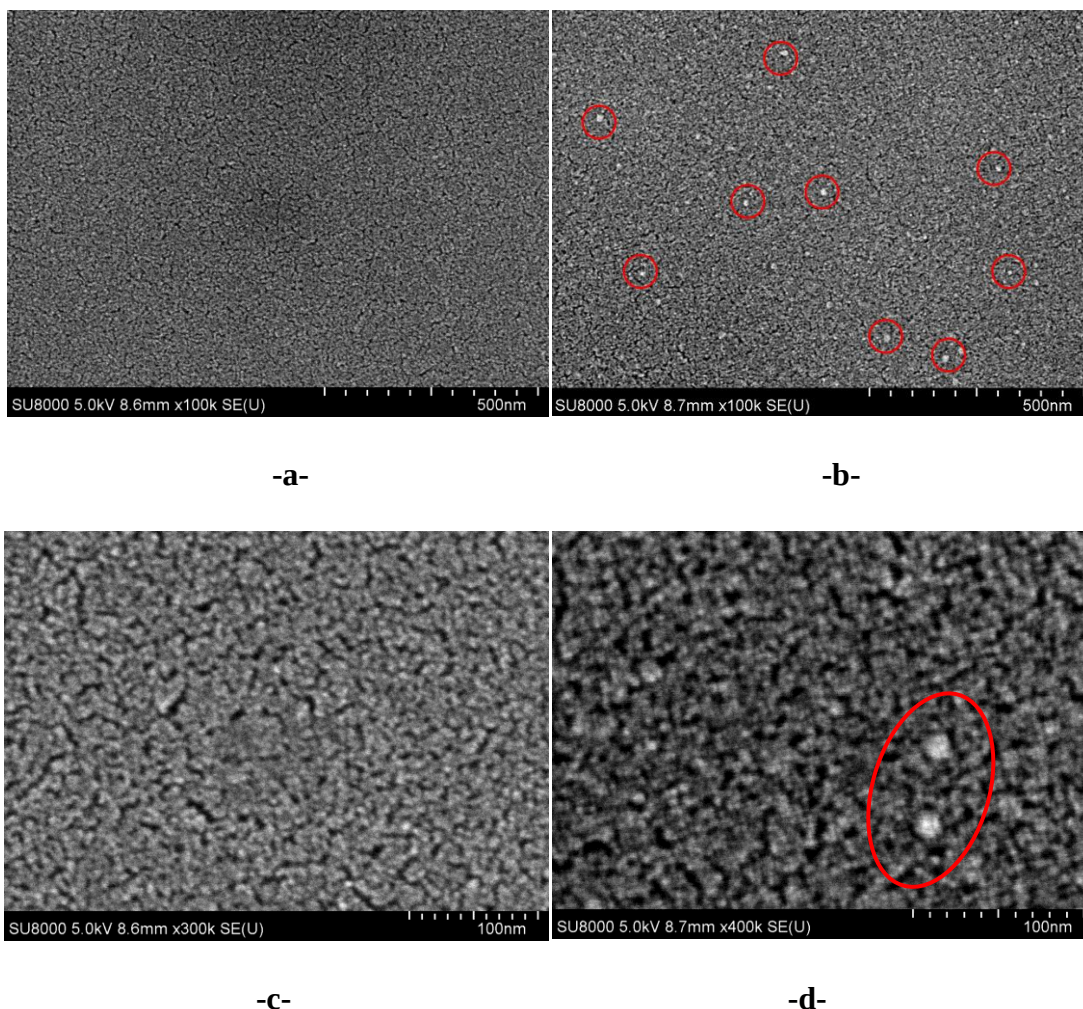


Figure 3.7 SEM micrograph of sample prepared using **a)** 500 mg and **b)** 800 mg of concentrated nitric acid **c)** and **d)** magnified images of panel a) and b), respectively.

From the combination of all XRD, N₂ sorption, UV-visible absorption measurements and SEM analysis; the safe zone for the acid amount is determined to be between 300 and 500 mg. In order to obtain the best liquid crystalline order, 500 mg of acid is decided to be the optimum amount for acidifying the initial solution.

3.2. Determination of the optimum metal salt to C₁₂EO₁₀ mole ratio

In the previous section, all the samples were prepared with a constant amount of Co(II) and Ti(IV) in order to see solely the effect of the acid on the mesophase order. Another important parameter, just as the acidity of the initial solution, is the loadable amount of metal salt in the mesostructured liquid crystalline network. MASA synthesis implies that the salt is melted upon the confinement into very small domains in the hydrophilic domains of the mesophase. One of the phenomenal aspects of MASA synthesis is that; under the guidance of the micellar

domains, restrained into very small volumes, the molten salt does not recrystallize even at cryogenic temperatures. [31] The more salt is added into the system, the thicker the molten salt + titania source layer and consequently, the walls will get. Normally, a lyotropic liquid crystalline (LLC) phase has two degrees of freedom; surfactant concentration and temperature. Here, the temperature is not in the concern because all the labor has been done at room temperature. However, the concentration of surfactant molecules is a variable that is often changed for experimentation. The driving force for LLC formation is the hydrophobic forces among alkyl tail groups and hydrogen-bonding network in the hydrophilic domains of the surfactant molecules. This constitutes the source of the attractive forces that hold the micelles together arranged in such geometry as cubic, hexagonal...etc. However, after a decrease in the surfactant concentration upon adding more liquid, i.e. molten salt, the attractive forces start to weaken and the d-spacing in the liquid crystalline phase expands. XRD used at small angles is useful tool for keeping track of such expansions or shrinkages. An experiment using 6 as-prepared thin film samples with different salt:C₁₂EO₁₀ ratios have been examined. **Figure 3.8** shows the small angle XRD patterns of the samples, prepared using 1:7, 2:7, 3:7, 4:7, 5:7 and 6:7 salt:surfactant mole ratios.

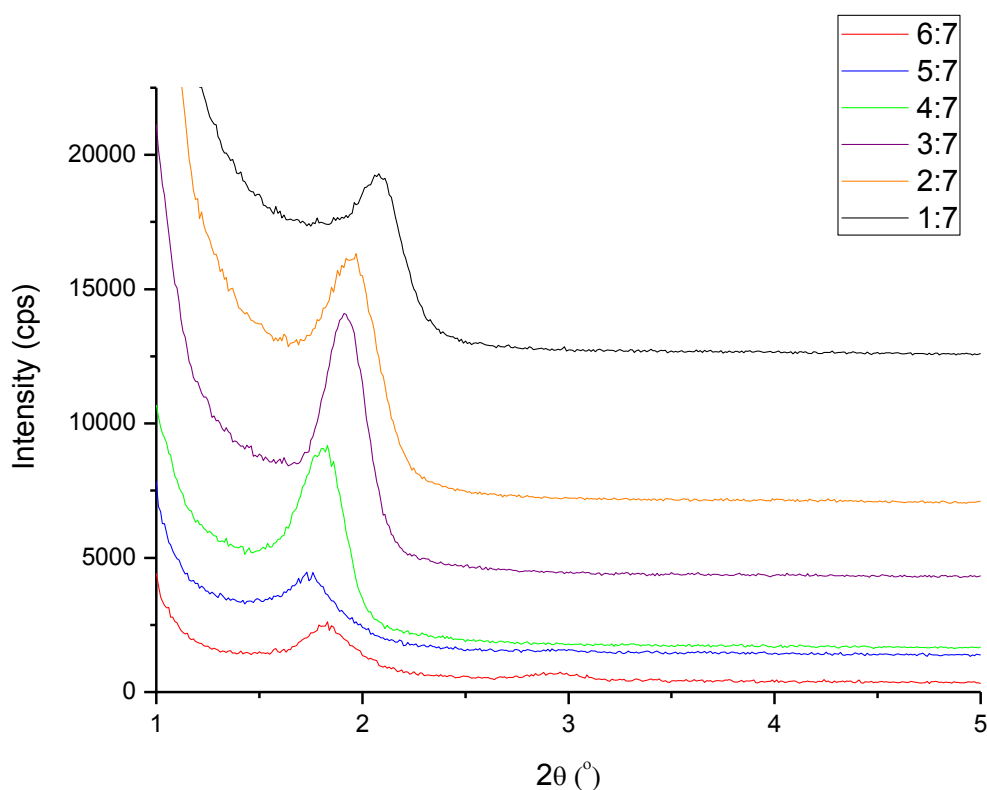


Figure 3.8 The small angle XRD patterns of samples, prepared using different amount of salt (as marked, salt:surfactant mole ratio).

The XRD patterns, in **Figure 3.8**, show that each sample exhibits a liquid crystalline order regardless to their salt:C₁₂EO₁₀ mole ratio. On the other, there is a clear deviation in the d-spacing of the mesophase. From Bragg's law, lattice parameter of each sample has been calculated and tabulated in **Table 3.1**.

Table 3.1: The Bragg angle and the d-spacing values of the samples prepared using different salt:C₁₂EO₁₀ mole ratio.

	Salt: C ₁₂ EO ₁₀ 1:1	Salt: C ₁₂ EO ₁₀ 2:1	Salt: C ₁₂ EO ₁₀ 3:1	Salt: C ₁₂ EO ₁₀ 4:1	Salt: C ₁₂ EO ₁₀ 5:1	Salt: C ₁₂ EO ₁₀ 6:1
Bragg Angle (°)	2.17	2.00	1.95	1.80	1.75	1.80
d-Spacing (Å)	40.6	44.1	45.3	49.0	50.4	49.0

The XRD patterns (**Figure 3.8**) and d-spacing values (**Table 3.1**) confirm the expansion behavior of the inter-micellar distances. A direct proportion exists between the d-spacing and the amount of salt in the mesophase. On the other hand, this trend breaks when the salt:C₁₂EO₁₀ ratio is 6:1 because the d-spacing is smaller than 5:1 and the same as 4:1 ratio. The reason is that the salt added into the system is no longer 100 % part of the mesophase. However, some proportion leaches out and form bulk salt crystals on the surface of the film. To confirm that, XRD patterns in the wide angles ($2\theta = 10^\circ$ to 80°) have also been collected (**Figure 3.9**).

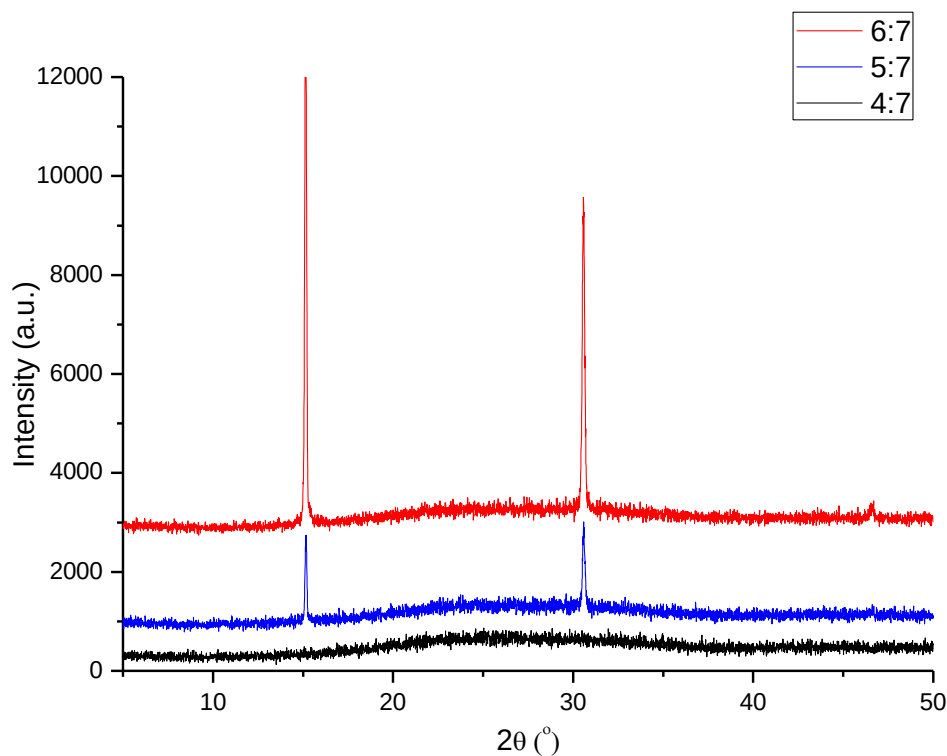


Figure 3.9 XRD patterns of 3 samples prepared with different amount of salt.

Instinctively, the XRD pattern of a pure LLC will exhibit no crystalline order on the atomic level, which means, it should exhibit amorphous properties, no diffraction lines are observed as wide angles. However, two sharp peaks attributed to the crystallographic planes of a hydrous form of $\text{Co}(\text{NO}_3)_2$ are present in the patterns of 5:1 and 6:1 salt: $\text{C}_{12}\text{EO}_{10}$ ratios. This data is in a good agreement with the fact that a layer of bulky crystalline islands is formed in the samples with 5:1 and 6:1 ratios, but not in the 4:1 ratio. **Figure 3.9** is a depicted demonstration of the possible behavior of the mesophase upon the increase of the salt: $\text{C}_{12}\text{EO}_{10}$ ratio.

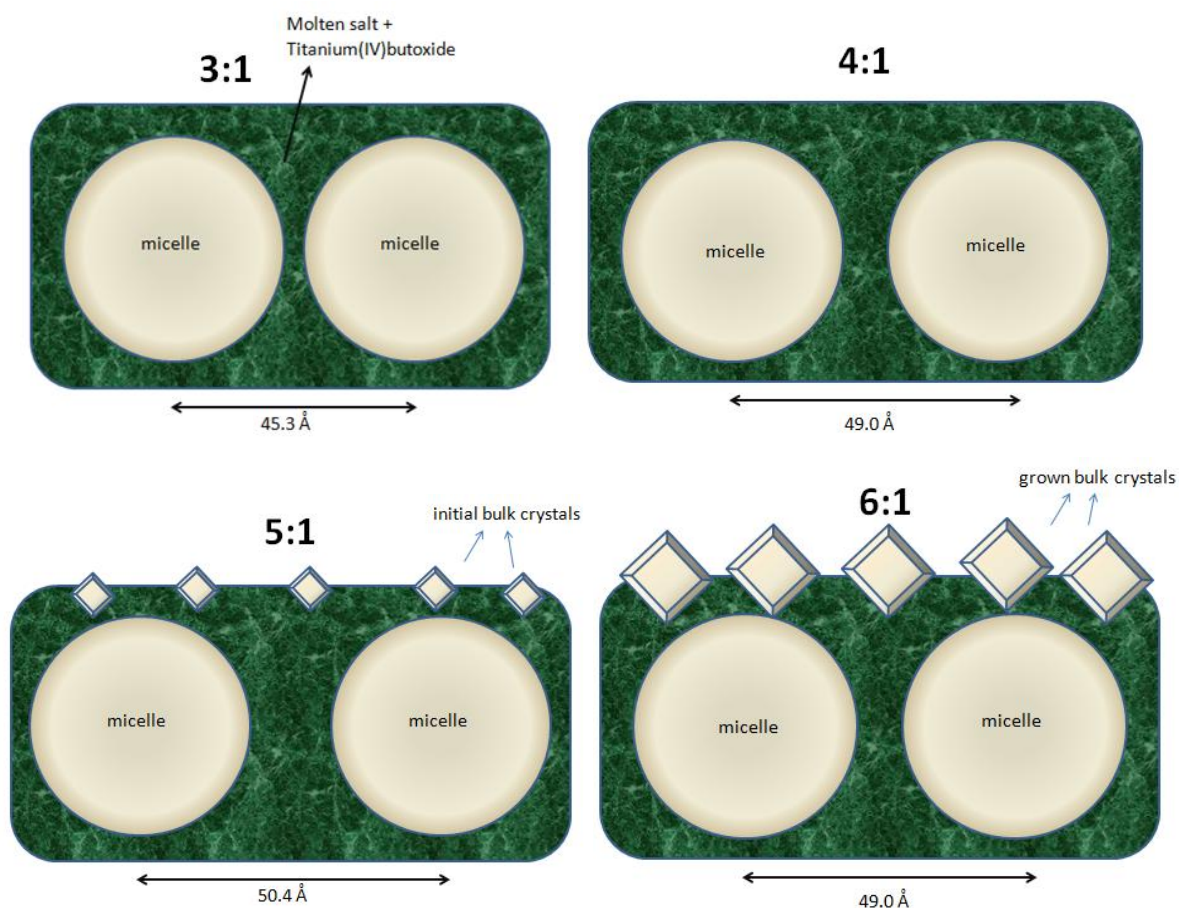


Figure 3.10 The behaviour of the mesophase upon the increase of the salt: $C_{12}EO_{10}$ ratio.

Analogous to a solution, the liquid crystalline phase gets saturated at the point where the salt: $C_{12}EO_{10}$ ratio is over 4:1 and supersaturated near 5:1 and initial crystal seeds start to appear at exact 5:1. Following that, the excess salt is totally crystallized at 6:1 and the mesophase returns to its initial saturated point similar to 4:1 but with undesired bulky salt crystals on top of the film. This shows that the 4:1 salt: $C_{12}EO_{10}$ ratio is the maximum ratio for a stable liquid crystalline phase. **Figure 3.11** shows the small angle XRD pattern of the sample prepared using 4:4:1 salt:titania source: $C_{12}EO_{10}$ molar ratio. Keeping the molar ratio of the metal salt to titania to 1 is important to obtain stoichiometric $CoTiO_3$.

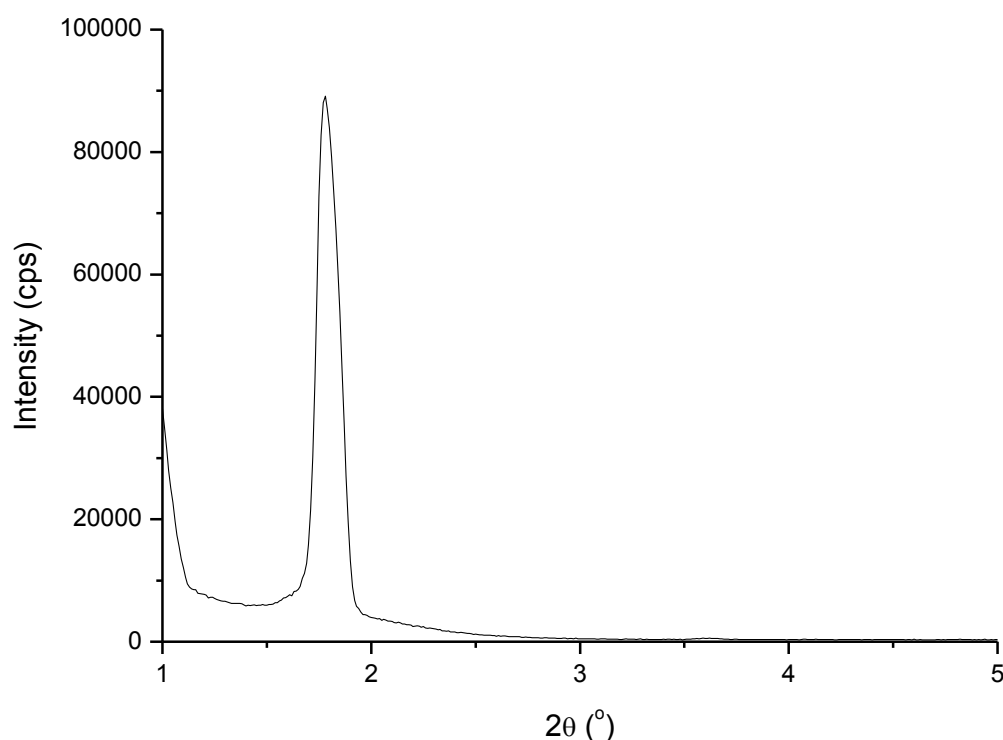


Figure 3.11 The small angle XRD pattern of the as-prepared sample using 4:4:1 Co:Ti:C₁₂EO₁₀ molar ratio.

The relatively sharper peak at $2\theta = 1.80^\circ$ in the small angle XRD pattern in **Figure 3.11** belongs to a well-ordered LLC phase. When compared to the sample with 4:7 Co:Ti ratio with its XRD pattern in **Figure 3.8**, it is realized that the d-spacing did not change. This data also indicates that the titania amount does not affect the inter-micellar distance because titania domains are weakly charged and already hydrolyzed and undergone condensation reaction, such that it does not occupy as much space in the hydrophilic domains of the mesophase. However, the effect of the Co(II) amount on the LLC structure has been seen clearly. In the samples which have Co:Ti mole ratio more than 1, based on the comparison of **Figure 3.8** and **Figure 3.11**; the orientation is lower because the diffraction intensity is lower. Grazing incidence small angle x-ray scattering (GISAXS) has been employed in order to confirm the LLC orientation (**Figure 3.12**).

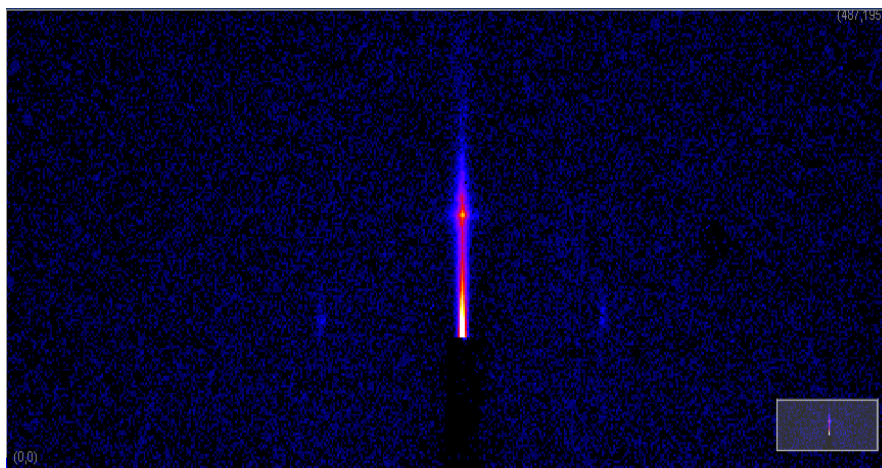


Figure 3.12 GISAXS pattern of the as-prepared sample using 4:4:1 Co:Ti: C₁₂EO₁₀ molar ratio.

In **Figure 3.12**, the single bright spot on top of the stopper attributed to the out-of-plane orientation and two symmetrical weaker spots on the sides attributed to the in-plane orientation. The position of the spots is the fingerprint of a hexagonal-closed-packed (*hcp*) crystal structure observed in a GISAXS pattern.

In this study, 4:1 salt: C₁₂EO₁₀ mole ratio is considered to be an ideal and safe composition for a pure mesophase without any bulk formation. In the light of this valuable data, all the studies about CoTiO₃, MnTiO₃ and Li₄Ti₅O₁₂ were carried with this optimum 4:1 salt: C₁₂EO₁₀ ratio.

3.3. Calcination of LLC Thin Films

In the previous two sections the importance of the acidity and salt concentration of the initial solution have been extensively discussed. Each parameter is proven to be very important for the order of the mesophase. In this section, the calcination process will be emphasized by means of setting the calcination temperature and time for the perfect final product. In fact, the calcination process is the step where the as-prepared liquid crystalline film consisting of surfactants, molten salt and titania domains become an actual mesoporous metal titanate thin film. Because all the synthesis happens at this point, the optimization of calcination temperature and time is of great importance.

3.3.1. Calcination Temperature

Generally, the term calcination is referred to a heating process where the sample gets rid of all of its combustible, decomposable and volatile components. In the MASA synthesis, all the raw materials of the as-prepared products are either burnable or volatile such as organic molecules (surfactants), nitrates (metal salts), alkoxides (titania source) and water (coming from the hydrous salt and air). Upon heating, basically all the anions are exchanged with oxygen to form the oxide of the concerning cation. The water and the residual ethanol evaporate; the carbonaceous compounds such as $C_{12}EO_{10}$ and CTAB are burned out and leave the structure as CO_2 or CO gases. $[Co(H_2O)_6](NO_3)_2$ or $[Mn(H_2O)_4](NO_3)_2$ or $LiNO_3$ and $(Ti(OC_4H_9)_4)$ disassociate, react with oxygen and form the metal titanates. Considering all these processes, choosing the right calcination temperature is a delicate work. It must be high enough in order to burn out the surfactant and yet, it should be kept at its minimum to obtain a thin-walled mesoporous structure. Because further heating will cause further crystallization, in the case of mesoporous materials, sintering of the grains should be restrained. The effect of calcination at higher temperatures or additional annealing after the calcination on the mesostructure of $CoTiO_3$, $MnTiO_3$ and $Li_4Ti_5O_{12}$ will be discussed later. In this section, UV-visible absorption and Raman spectroscopy are employed to find the minimum temperature required for the metal-titanate formation. $[Co(H_2O)_6](NO_3)_2$ is chosen for the metal source and the formation of $CoTiO_3$ is tracked using UV-visible absorption spectroscopy (**Figure 3.13**). A sample with $Co:Ti:C_{12}EO_{10}$ ratio of 4:4:1 has been prepared in order to observe the cobalt titanate formation. The as-prepared film is put into an oven at $140\text{ }^{\circ}C$ and left there for 20 min.. The experiment is continued by heating the sample up to $180\text{ }^{\circ}C$ and annealing for another 20 min. Finally, the same procedure is followed by another annealing process at $220\text{ }^{\circ}C$ and a UV-visible absorption spectrum is collected at each temperature step.

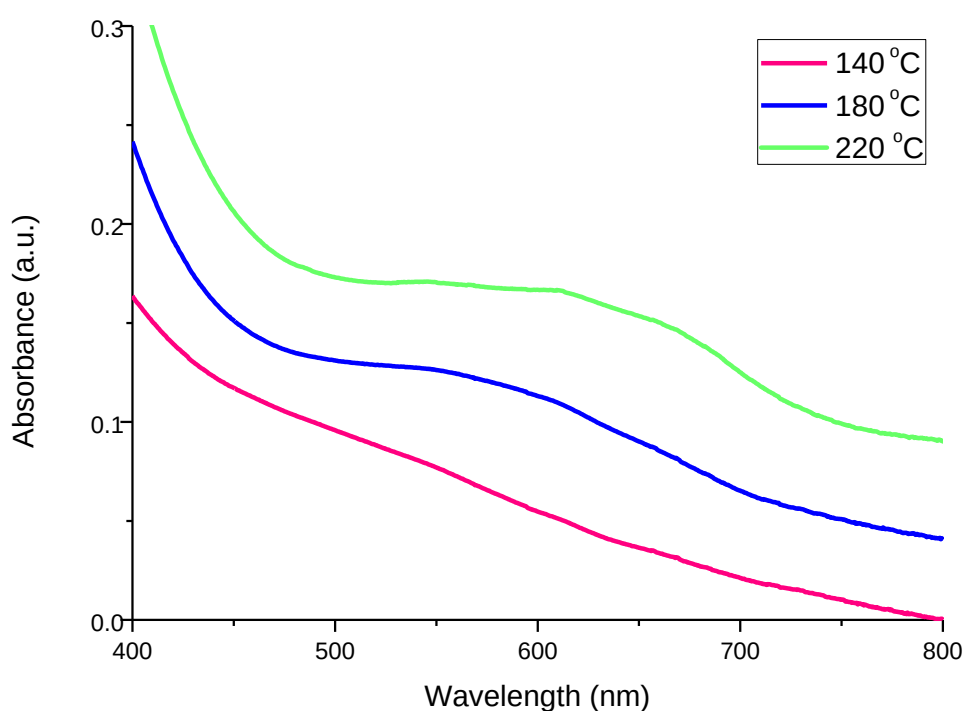


Figure 3.13 Visible absorption spectra of Co(II)-Ti(IV) sample at different temperatures (as marked).

In **Figure 3.13**, the visible absorption spectrum of the Co(II)-Ti(IV) sample heat treated at 140 °C, then annealed at 180 °C and 220 °C in the wavelength range of 400-800 nm are presented all together. The colors of the spectrum lines are representative to their optical appearances. At 140 °C, the sample exhibits a broad absorption nearly through the all visible region except in the red and in the blue region. This optical absorption behavior gives the sample its violet color. Usually, the violet color appears in Co(II) containing ionic solutions when Co^{2+} is coordinated with water molecules in an octahedral symmetry. This shows that the sample still contains some amount of water and the Co^{2+} ions have not yet reacted with anything. Going through 180 °C, the absorption in the blue region decreases and the sample becomes blue. This is attributed to the decrease of energy in the d-d transitions when Co^{2+} is coordinated with a halogen anion such as Cl^- , Br^- , *etc*, in a tetrahedral symmetry. At this step, the major part of the water is evaporated and Br^- , which is present due to CTAB- becomes dominant over water. However, at 220 °C a similar spectrum to the one in **Figure 3.6** is observed which was attributed to CoTiO_3 . It seems that the calcination becomes effective at this temperature and therefore the synthesis of CoTiO_3 starts. Based on the brief visible absorption data, 220 °C is the temperature where CoTiO_3 is formed or started to form. It is

useful to detect the synthesis temperature of metal titanates in the mesostructured phase however; the knowledge of how much surfactant is burned cannot be predicted from visible absorption spectra. However, Raman spectra of a similarly heat treated Co(II)-Ti(IV) sample at different temperatures are also collected (**Figure 3.14**) for contributive information.

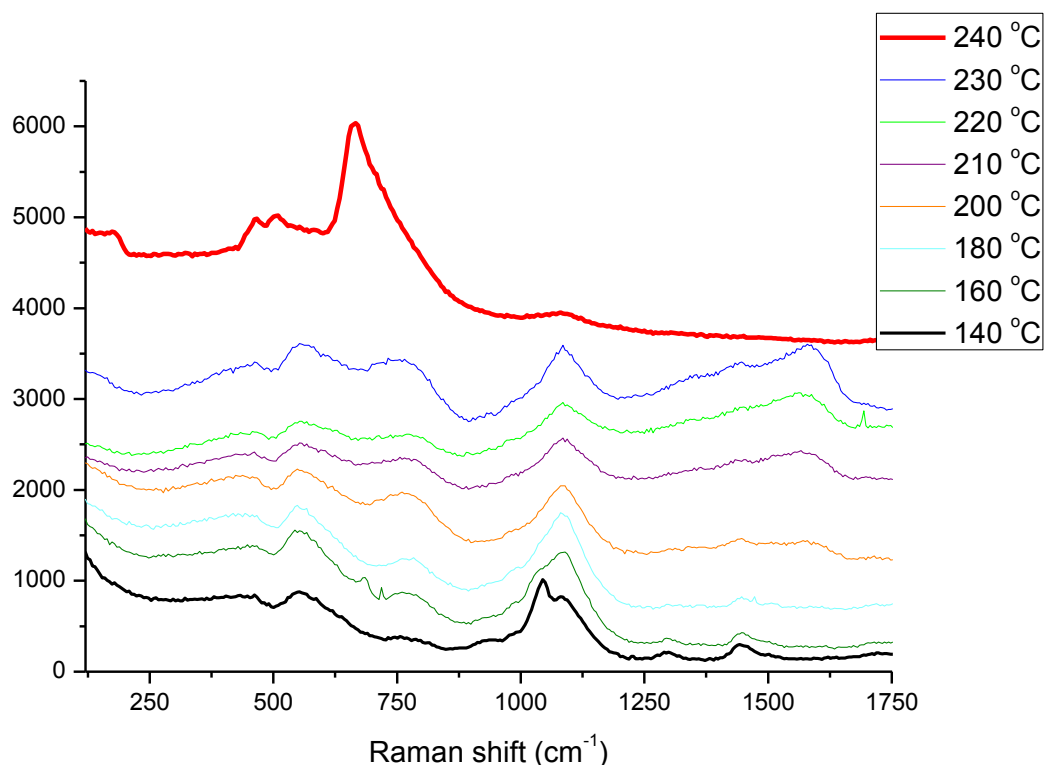


Figure 3.14 Raman spectra of Co(II)-Ti(IV) sample at different temperatures

The Raman spectra shown in **Figure 3.14** belong to a single sample heat treated at increasing temperatures from 140 to 240 °C. It is seen that the material exhibits similar properties up to 230 °C where there are mostly noise related broad peaks with no significant information about the formation of CoTiO_3 . This shows that no crystallization occurred in the sample and probably surfactant domains are still present. But then, the spectrum changes drastically at 240 °C where some peaks observed at 473, 511 and 676 cm^{-1} which are attributed to the E_g , T_{2g} , and A_{1g} , Raman-active modes of the crystalline Co_3O_4 . [72] According to Raman spectra, the first metal oxide forms at 240 °C which is not in agreement with 220 °C, the formation of CoTiO_3 , detected from the visible spectra. The reason of the detection of two different materials in two different spectroscopic methods is that some small amount of Co_3O_4 is simultaneously formed with CoTiO_3 , which is probably in total amorphous structure, hence, undetectable via Raman. It will be shown later that the Raman spectrum of CoTiO_3 will reveal

when the thin film sample -calcined at higher temperatures- is scraped from the glass surface. Otherwise, the formation of Co_3O_4 in the CoTiO_3 sample will be further explained in the next sections. Although, it is for now enough to point that the Co_3O_4 formation is an evidence for CoTiO_3 formation and, the Co_3O_4 crystals are in minority compared to CoTiO_3 . The green color of the optically transparent thin film and the characteristic visible absorption spectrum of the sample prepared with 4:4:1 $\text{Co(II):Ti(IV):C}_{12}\text{EO}_{10}$ ratio is a strong evidence that minor Co_3O_4 crystals are quite small and probably formed on the surface of the mesoporous CoTiO_3 thin film during calcination.

In the light of these valuable spectroscopic data, the minimum temperature required for metal titanate formation is found to be 240 °C, which is in a good agreement with the work of Karakaya *et al.* [33] where they found the formation temperature of mesoporous zinc titanate as 250 °C. It also shows that, metal nitrate salts having similar melting points, follow similar metal titanate formation routes. Concordantly, a temperature in the safe zone is chosen for all three metal titanates, known to be enough to burn all the surfactants by leaving behind the mesoporous CoTiO_3 or MnTiO_3 or $\text{Li}_4\text{Ti}_5\text{O}_{12}$; 350 °C is chosen to be an appropriate calcination temperature for those three metal titanates. The lower limit of the safe zone for the calcination temperature is the range where the minimum required temperature for burning the surfactant and forming the metal titanate. The upper limit is considered to be the maximum acceptable temperature where no further crystallization and breakdown in the mesoporous structure occurs. The importance of the breakdown in the mesoporous structure will be emphasized in the section 3.4. Also, the maximum acceptable temperature for an efficient calcination is important for kinetic reasons. As it is well known that the calcination process runs faster at higher temperatures; in other words, the calcination time can be kept at its minimum upon increasing the calcination temperature. This will be covered in the following section.

3.3.2. Calcination Time

As for calcination temperature, the time required for an ideal calcination is also an important parameter. Conventionally, as described before, calcination is a heating process where all the burnable and volatile components of the sample are burned out and volatilized. However, in MASA technique, the calcination step is the heart of the synthesis itself. The calcination time is a key parameter, which dictates not only the burning and/or volatilizing the concerning components, but also the formation, growth, and crystallization of the mesoporous metal titanate.

MASA can be considered as a soft-templating method at molecular level. The small micelle size due to shorter alkyl chains of the surfactant molecules is another aspect of MASA, which differs from other soft-templating methods using large co-polymers. The molecular self-assembly phenomenon is a superior to the other templating methods and yet, a very delicate process, where the molten salt and hydrolyzed titania are guided by micelles made of two different surfactant molecules. They assemble together to form LLC mesophase upon coating the substrate. This mesophase constitutes the preliminary step to mesoporous metal oxide synthesis and it is quite stable over time. However, there are some obstacles in maintaining the LLC phase stable for long periods, such as, salt leaching out of the mesophase to form bulk salt crystals on top of the film is problematic. Optimization studies of the salt to surfactant ratio in order to keep the LLC phase stable over time, have been explained in **section 3.2**. However, when it comes to stability over time, one should be more specific about the duration. The XRD data showing that the sample prepared using 4:1 salt: C₁₂EO₁₀ ratio, which does not have any leached out and crystallized salt, corresponds to the XRD pattern, run approximately 30 min after the spin coating. For some applications, 30 min might not be enough. In order to check the stability of the as-prepared samples in longer times, a sample with 4:1 salt: C₁₂EO₁₀ ratio has been prepared. An XRD pattern is obtained right after spin coating and another after 6 h of an ageing process at room temperature. **Figure 3.15** shows how the XRD pattern of the sample prepared with 4:1 salt: C₁₂EO₁₀ ratio, changes by 6 hours after preparation.

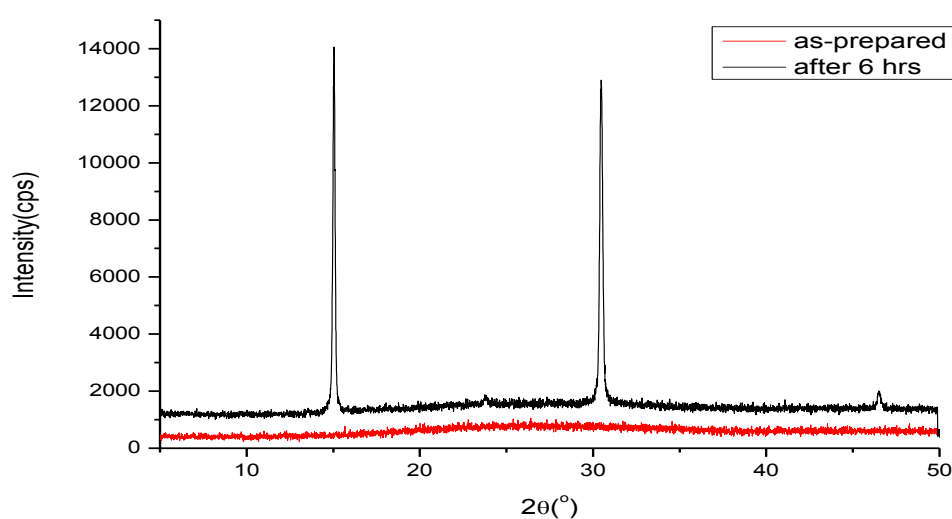


Figure 3.15 Time dependent XRD patterns of the as-prepared sample with 4:1 salt:C₁₂EO₁₀ ratio.

In **Figure 3.15**, the XRD pattern of the sample aged for 6 hrs at room temperature shows that there has been some crystallization due to the leached out salt. Those bulky salts are usually formed on top of the film and they are detectable under an optical microscope. **Figure 3.16** is an OM image of an as-prepared sample intentionally prepared with a high salt: $C_{12}EO_{10}$ ratio and low amount of acid in order to accelerate the bulk salt crystallization process and obtain more visible crystal domains.

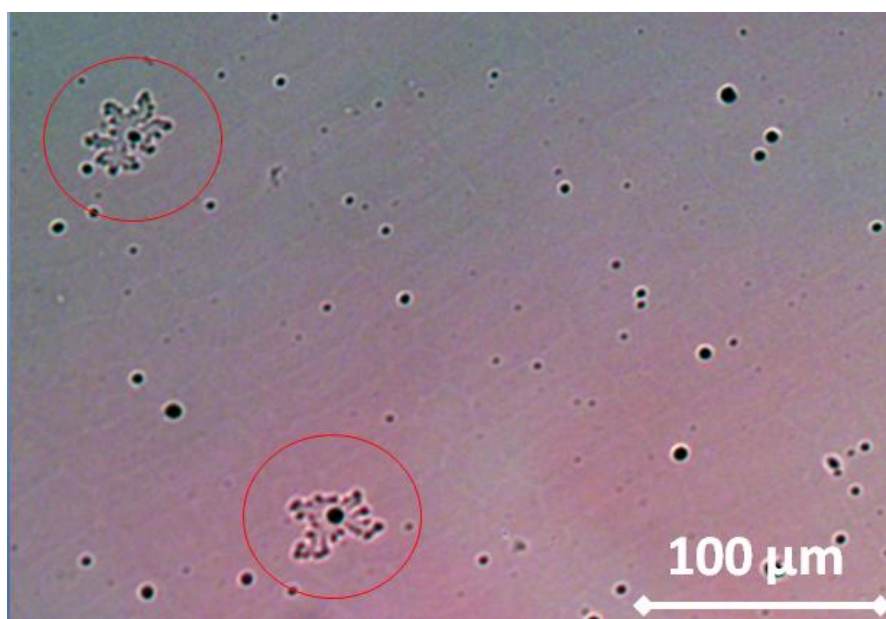


Figure 3.16 OM image showing the crystal growth of the salt species (circled in red).

It should be also noticed that the crystal growth observed in **Figure 3.16** started from defective points and continued growing to form islands with radius nearly 50 μm . As it is known from all crystal growth or film deposition techniques, defect centers are preferable locations for crystal growth. The OM image also emphasizes the importance of the substrate quality for a clear and stable film in LLC phase.

The Co(II) salt crystallizing on the surface of the film is disadvantageous in many terms. Bulky salt crystals on top of the film make the transparency of the film loose in the progress of time. The film becomes opaque, a property that is not desired for most of the applications. On the other hand, the opaqueness (or transparency) of the sample can be easily inspected by naked eye. **Figure 3.17** is a photograph of both totally transparent and partially opaque sample.



Figure 3.17 Photograph of a transparent vs. opaque film.

The opaque sample contains a lot of salt crystals which will later form, upon calcination, bulk Co_3O_4 domains. The formation of bulk Co_3O_4 in CoTiO_3 mesoporous thin films is studied extensively and therefore; it should be discussed under a separate head line, because it is highly related with the calcination route (i.e. calcinations time, pre-calcination. and annealing etc).

3.3.3. Formation of bulk Co_3O_4 in CoTiO_3 mesoporous thin films

The first sign of Co_3O_4 formation in CoTiO_3 mesoporous thin films were obtained in the Raman study of the formation temperature of CoTiO_3 (**Figure 3.14**). However, other evidences showed that Co_3O_4 is formed only on the surface of the film and CoTiO_3 still dominates the majority of the synthesized material. Raman spectroscopy, XRD, SEM, EDX elemental mapping and TEM have been employed in order to characterize the formation of Co_3O_4 .

3.3.3.1. Raman spectroscopy

3.3.3.1.1. Determination of the phases

Raman spectra have been collected for two samples prepared using the same 4:4:1 Co:Ti: C₁₂EO₁₀ mole ratio and calcination temperature of 350 °C using different calcination routes. The first sample has been calcined slowly, heated up to 350 °C from room temperature with a temperature gradient of 1 °C/min and left at that temperature for 1.5 hrs. The second sample is put into the oven already heated to 350 °C and left calcining for only a few minutes. **Figure 3.18** shows the Raman spectra of both samples taken from the surface of the films. The same samples were then scraped and **Figure 3.19** shows the Raman spectra of both samples in the powder form.

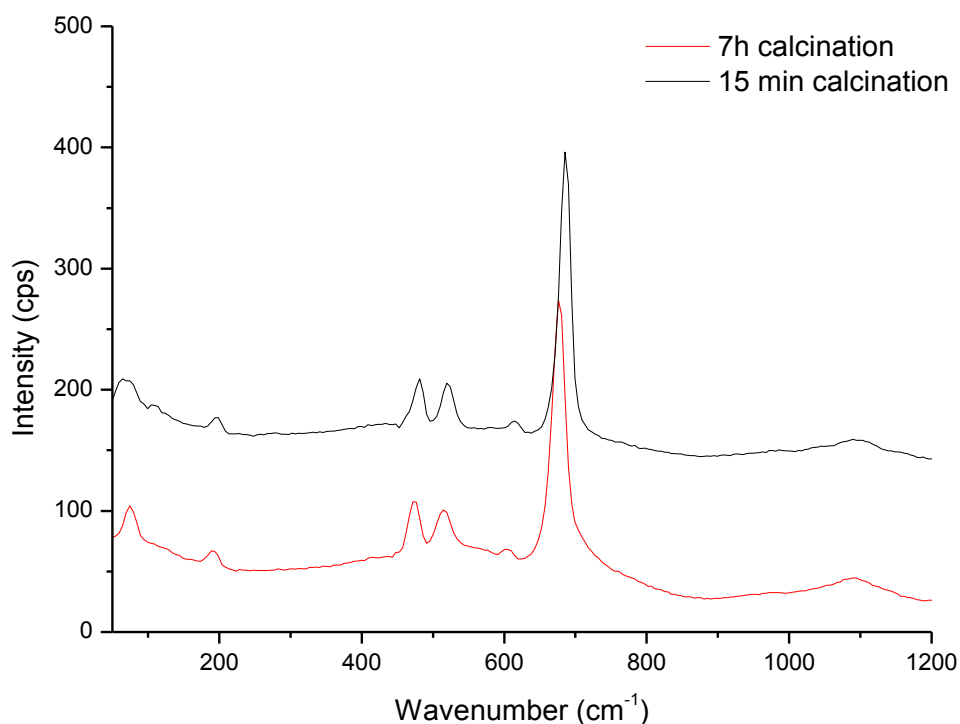


Figure 3.18 Raman spectra recorded from the surface of CoTiO₃ films calcined for 7 hrs and 5 min.

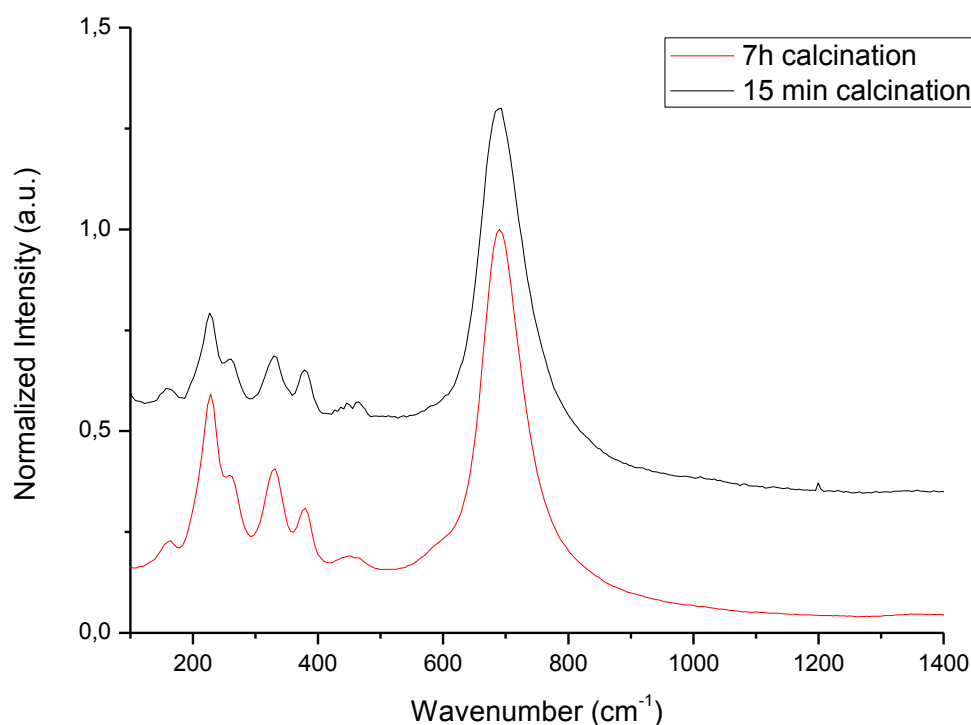


Figure 3.19 Raman spectra recorded from the scraped powder of CoTiO₃ samples calcined for 7 hrs and 15 min.

Valuable information can be extracted from the spectra shown **Figure 3.18** and **Figure 3.19**. First, it is possible to suggest that there is no significant distinction between the Raman spectra taken from the surface of the sample and its powder form of the two samples. This proves that even the calcination time is decreased from 7 hrs to a few minutes, the same product is obtained. Second, there is a clear distinction between to spectra obtained from the surface and the scraped powder of the materials. The peaks around 676, 610, 511, 480 and 191 cm⁻¹ in the first spectrum in **Figure 3.18** are attributed to the Raman-active modes of Co₃O₄. [73] On the other hand, the peaks around 694, 462, 383, 335, 265, 233 and 207 cm⁻¹ in the second spectrum in **Figure 3.19** are attributed to the Raman-active modes of CoTiO₃ which are in a good agreement with the reference data. [74] Therefore, from Raman measurements, it has been justified that the Co₃O₄ phase is less populated than the main CoTiO₃ framework and, Co₃O₄ crystals are formed on the surface of the film but not throughout the entire structure.

3.3.3.1.2. Origin of the Co_3O_4 formation in CoTiO_3

In the previous section, it has been shown that in samples prepared with compositional 4:4:1 Co:Ti: $\text{C}_{12}\text{EO}_{10}$ mole ratio, Co_3O_4 is formed in parallel with CoTiO_3 regardless of the calcination route. In this part, further investigation will be carried in the interest of the formation CoTiO_3 and hence, Co_3O_4 in different sample preparation and annealing conditions. The acidity of the initial solution and the Co:Ti or Co+Ti: $\text{C}_{12}\text{EO}_{10}$ ratio of the composition might be the factors affecting the microstructure of Co_3O_4 and its population. Acidity is an important parameter which dictates the size of the polymerized titania domains by effecting the hydrolysis and condensation of titanium(IV)butoxide in the initial solution. From this statement, it is expected that the Co-O-Ti bond formation will be encouraged if the polymerized titania domains are kept in the smallest size possible. An experiment has been carried out in order to observe the effect of acid in the solution, to the Co_3O_4 formation and its population in the CoTiO_3 matrix. 6 solutions with 7:7:1 Co(II):Ti(IV): $\text{C}_{12}\text{EO}_{10}$ molar ratio containing 500, 600, 700, 800, 900 and 1000 mg of acid, respectively, have been prepared. 6 samples prepared from each solution have been spin coated with the same spin speed and calcined at the same temperature of 350 °C using fast calcination route (kept at 350 °C for 15 min). Raman spectra of those samples are shown in **Figure 3.20** and **Figure 3.21**.

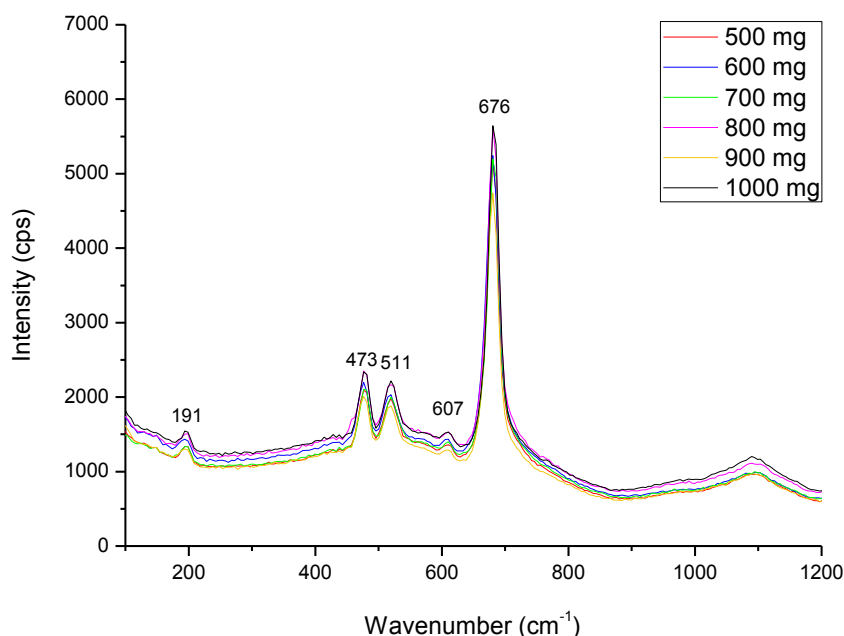


Figure 3.20 Raman spectra collected from the surface of the samples prepared with different amount of acid.

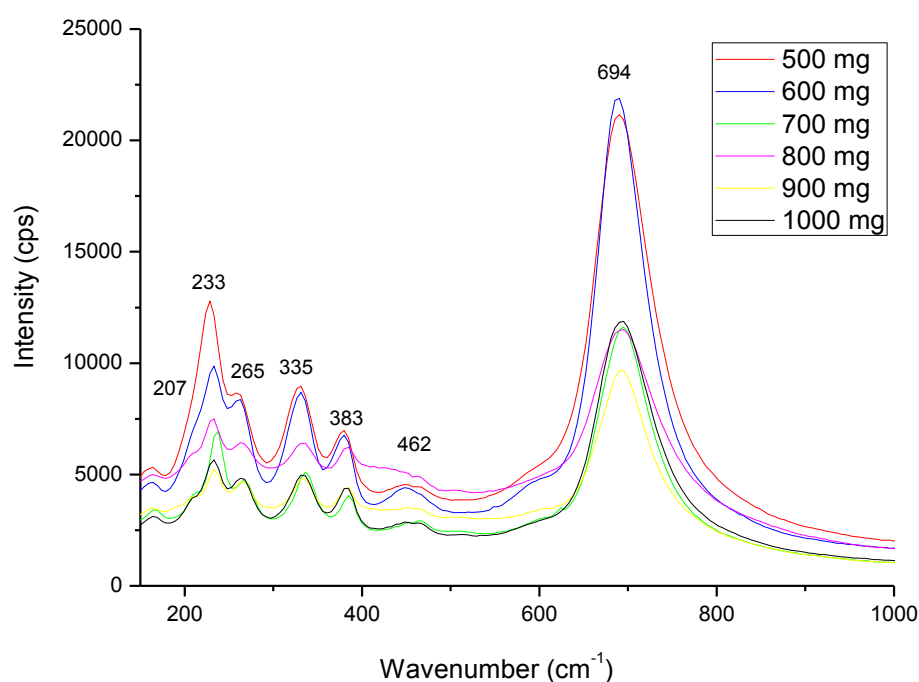


Figure 3.21 Raman spectra collected from the powder form of the samples prepared using different amount of concentrated nitric acid.

Raman spectra shown in **Figure 3.20** belong to the surface of the samples. It is clearly visible that all the films, no matter how much acid is added in their initial solutions, contain Co_3O_4 crystals on the surface, shadowing the Raman signals of CoTiO_3 . Besides, Raman spectra shown in **Figure 3.21** belong to the powder of the samples collected by scraping the film from the glass substrate. Those spectra, as specified before, belong to CoTiO_3 , and no remarkable difference is observed among the samples prepared with different amount of acid. On the other hand, the colors of the films slightly differ from each other due to the difference in the $\text{Co}_3\text{O}_4/\text{CoTiO}_3$ ratio. Naturally, CoTiO_3 is a green material. The mixture of CoTiO_3 and Co_3O_4 is the mixture of green + black which can be considered as dark green. This means that the darker the color of the film gets, the more Co_3O_4 is formed. This fact was already confirmed by visible absorption spectroscopy shown in **Figure 3.6**. It seems that the acid has an indirect role on the crystallization of Co_3O_4 by tuning the size of domain. This brings out new questions such as; does the initial titanium(IV)butoxide over Co(II) concentration or the cumulative amount of Co(II) and Ti(IV) over $\text{C}_{12}\text{EO}_{10}$ have an effect on the Co_3O_4 formation? In order answer these questions, several samples with different compositions have been prepared and their Raman spectra have been collected. **Figure 3.22** shows the Raman

spectra of the powder form of the films having different Co:Ti mole ratios. For 6 samples, Ti: C₁₂EO₁₀ ratio was kept constant meanwhile the molar ratio of Co:Ti increased gradually from 1:7 to 6:7. Because these are all scraped powders, it is expected to monitor the formation of CoTiO₃.

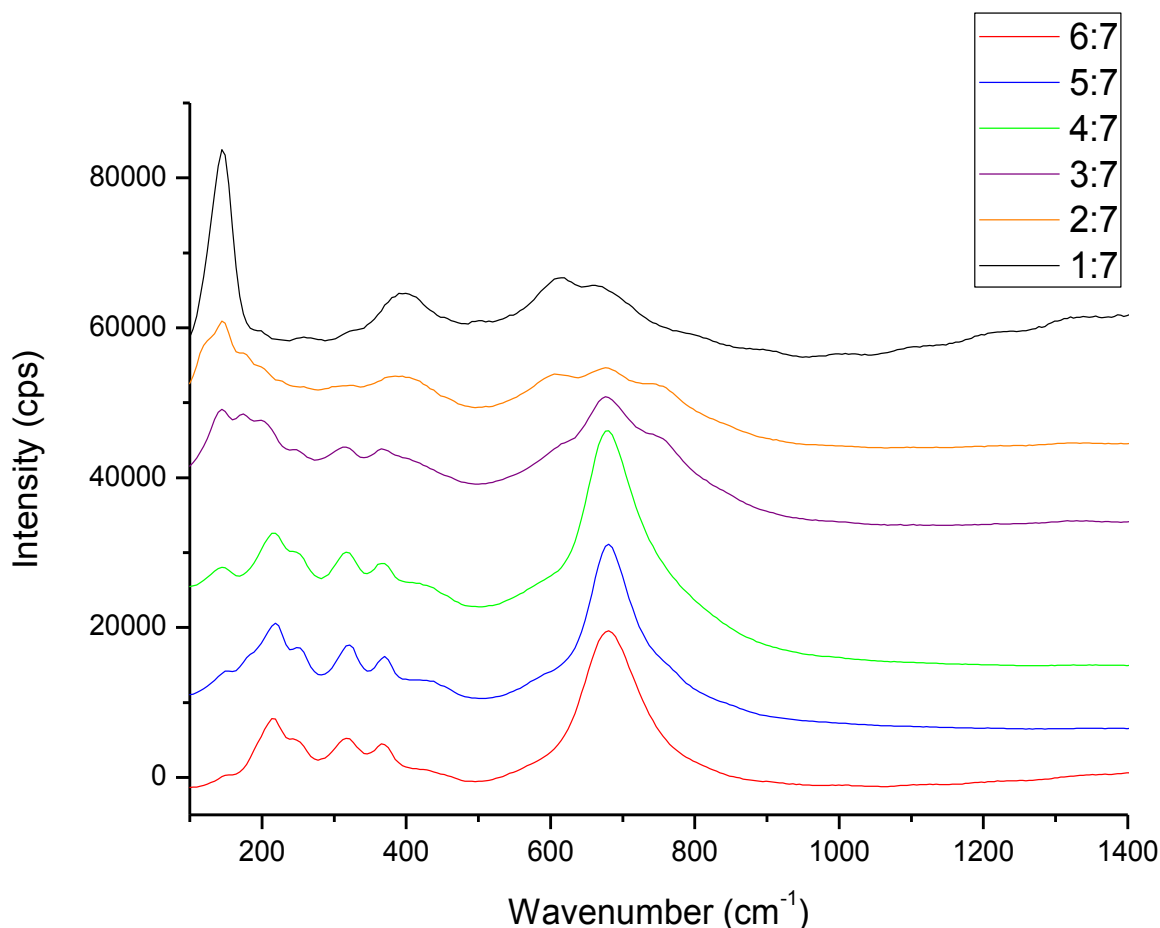


Figure 3.22 Raman spectra of the powder form of the films having different Co:Ti mole ratios (as marked).

The intense peak in the first spectrum around 150 cm⁻¹ and the other two peaks around 400 and 610 cm⁻¹ are attributed to the E_g, B_{1g} and E_g modes of anatase TiO₂. There is also a broad peak around 695 cm⁻¹, mixed up with high frequency E_g mode of anatase, belongs to CoTiO₃. At this point, the majority of the sample is in the anatase phase. The low frequency E_g mode of anatase around 150 cm⁻¹, is a good probe to follow the course of event in the structure. This particular characteristic peak loses intensity upon the introduction of more Co(II) in the system. The intensity of the peak continues decreasing up to 4:7 and disappears after 5:7 Co:Ti ratio. Meanwhile, the first noticeable spectrum where all the Raman modes of CoTiO₃ are observed belongs to the one with 4:7 Co:Ti ratio. From this point, CoTiO₃ becomes more

apparent when the Co:Ti ratio increases to 5:7 and 6:7. **Figure 3.23** shows the Raman spectra recorded from the surfaces of the samples of 4:7, 5:7 and 6:7 Co:Ti ratio.

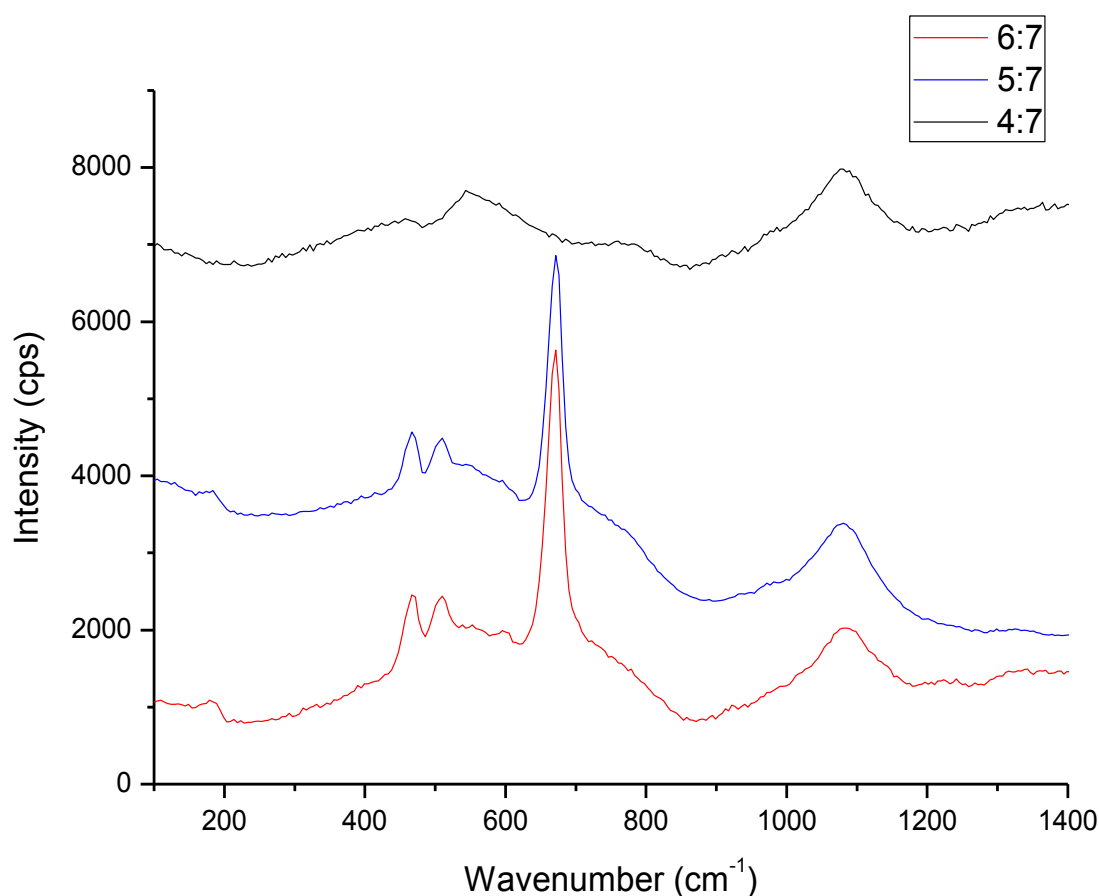


Figure 3.23 Raman spectra recorded from the surfaces of the samples prepared with 4:7, 5:7 and 6:7 Co:Ti mole ratio

The Raman spectra in **Figure 3.23** show that the Co_3O_4 formation starts when the ratio between Co and Ti exceeds 4:7. It has been already observed in the XRD patterns (**Figure 3.9**) that the cobalt salt leaches out from the mesophase to form bulky salt crystals after 5:7 Co:Ti mole ratio. In this context, there is strong evidence that the Co_3O_4 crystals detected by Raman in **Figure 3.23** are the products of the initial leached out cobalt salts. Consequently, these salts react with oxygen during calcination to form Co_3O_4 . On the other hand, the probability of having Co_3O_4 crystals not only on the surface of the film but also inside the matrix should not be excluded.

Another Raman study shows that, samples known to have no bulky salts leached out, also contains some Co_3O_4 . **Figure 3.24** shows the Raman spectra recorded from the surfaces of the samples prepared with 4:4:1, 5:5:1, 6:6:1 and 7:7:1 Co:Ti:C₁₂EO₁₀ mole ratio.

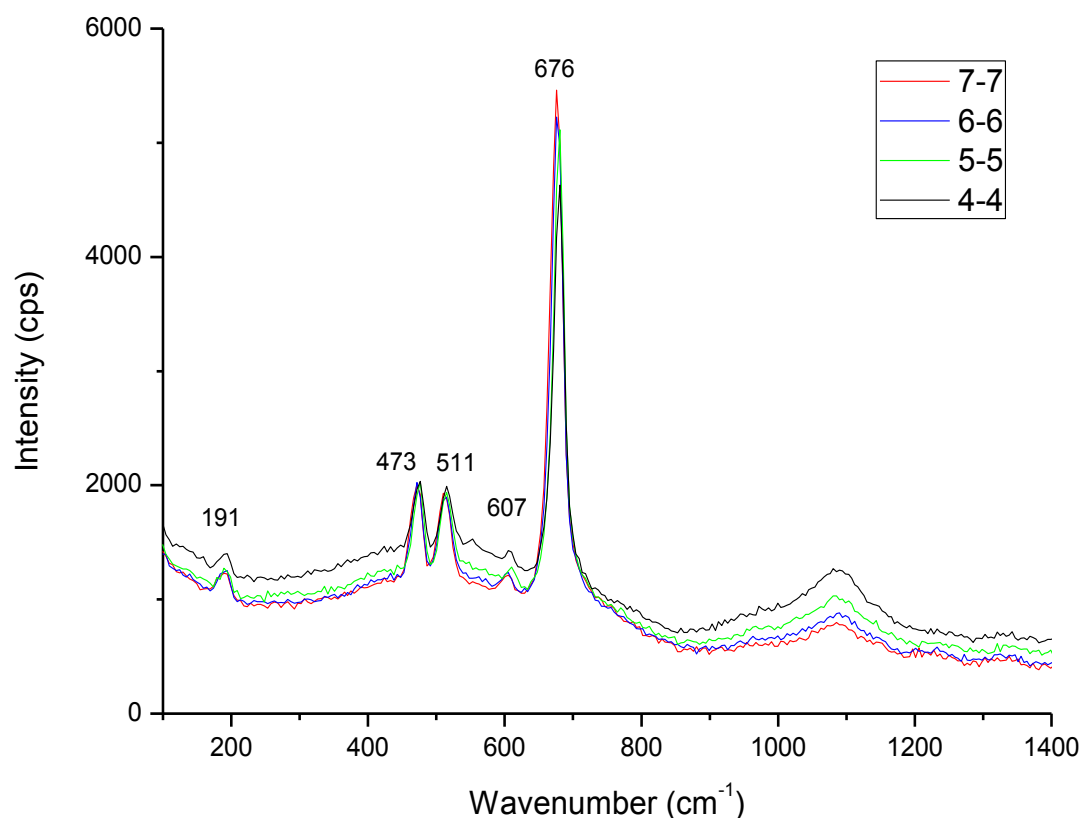


Figure 3.24 Raman spectra recorded from the surfaces of the samples prepared using different Co:Ti:C₁₂EO₁₀ mole ratios.

Interestingly, the Co_3O_4 is also observed in the sample prepared with 4:4:1 Co:Ti:C₁₂EO₁₀ mole ratio. However, in **Figure 3.15**, no XRD lines had been observed regarding to salt crystals from the as-prepared LLC sample, prepared with the same composition. The primary explanation would be; the leaching of the salt does not take place at room temperature but it may at higher temperature. This means that even the initial as-prepared film is free of bulky salts under ambient conditions, some cobalt salts may leave the mesophase to form salt crystals on the surface and these crystals might later form Co_3O_4 upon calcination. Considering that the LLC mesophase becomes unstable with increasing temperature, it is logical to speculate that the salt-loading limit of the mesophase decreases with increasing temperature. Another explanation can be; if the sample is initially stable, there might not be

any leaching at any temperature but, Co_3O_4 may somewhat form its own crystal domains incorporated inside the CoTiO_3 matrix. Further characterization using electron microscopy, supports the second explanation.

3.3.3.2. SEM and STEM elemental mapping

Raman spectroscopy and XRD are useful tools for phase characterization. On the other hand, it is difficult with these methods to extract information about the micro and nanostructure of the materials. In order to have deeper understanding on the formation of CoTiO_3 and its side product Co_3O_4 ; scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) have been used for microstructure characterization. It is not easy to observe the mesopores using an SEM instrument due to its upper resolution limitations especially when the material has pores with size less than 5 nm. However, SEM and STEM can provide satisfactory answers to the Co_3O_4 formation mystery. **Figure 3.25** is an SEM micrograph of a sample, prepared using 4:4:1 Co:Ti: $\text{C}_{12}\text{EO}_{10}$ mole ratio and spin coating on a silicon substrate at 1500 rpm. The sample has been lightly coated with Pt (kept in the plasma chamber for 10 s) in order to enhance the image quality.

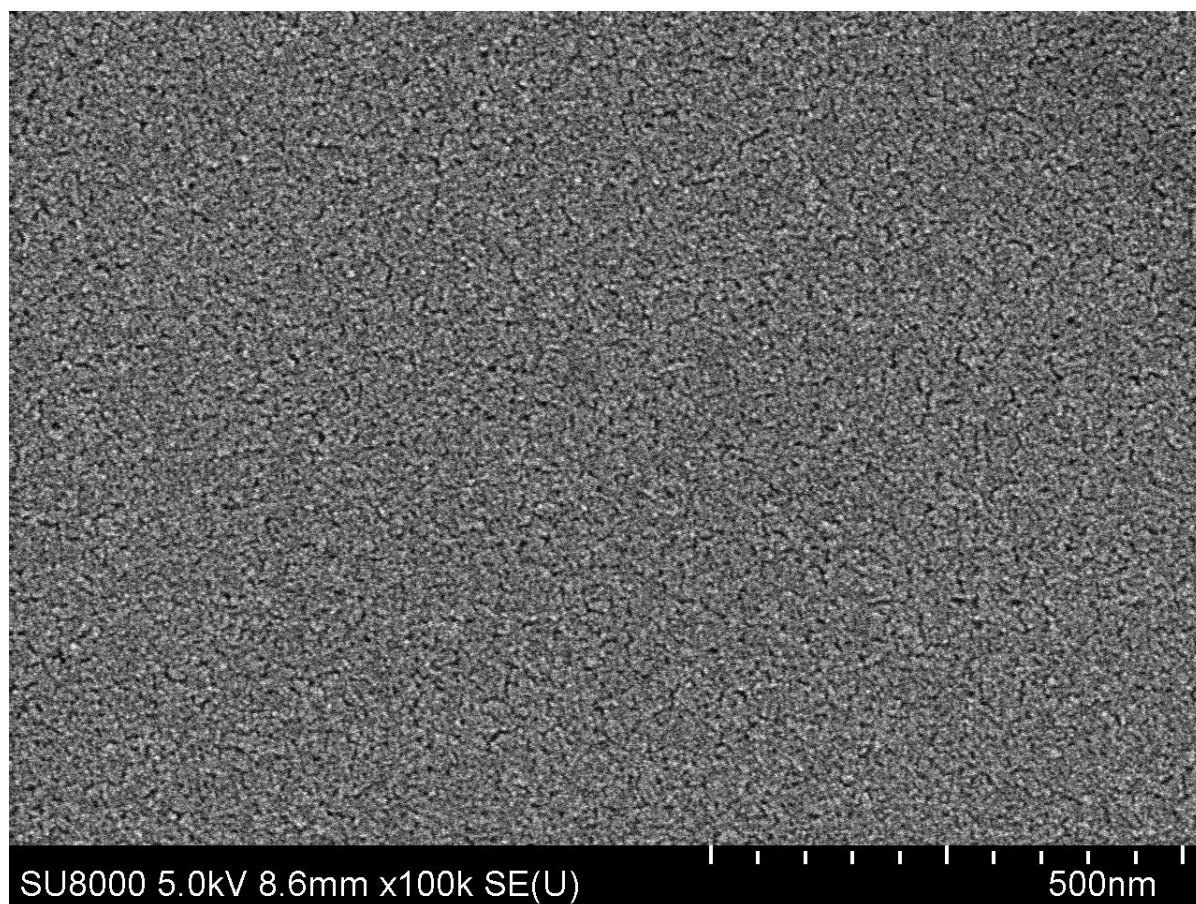


Figure 3.25 SEM micrograph of the sample prepared using 4:4:1 Co:Ti: $\text{C}_{12}\text{EO}_{10}$ mole ratio.

The SEM micrograph in **Figure 3.25** provides a general view of the mesoporous CoTiO_3 thin film. Other micrographs at higher magnifications are shown in **Figure 3.26**.

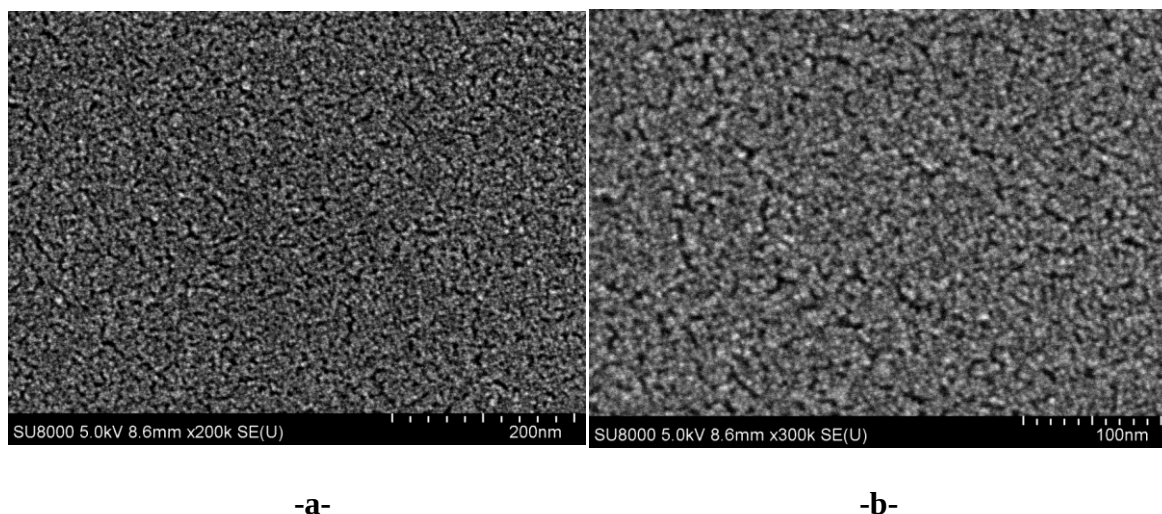


Figure 3.26 SEM micrograph of the sample prepared using 4:4:1 Co:Ti:C₁₂EO₁₀ mole ratio at magnifications **a)** $\times 200\text{k}$ and **b)** $\times 300\text{k}$

From all SEM micrographs shown in **Figure 3.25** and **Figure 3.26**, it has been observed that the mesostructure of CoTiO_3 thin film looks quite homogeneous and no big bulky crystals are formed on top.

STEM has also been employed in order to observe the microstructure of the mesoporous CoTiO_3 thin films. STEM is a special mode, which is available in some TEM instruments equipped with scanning coils and additional detectors similar to SEM. It can be simply described as the combination of an SEM and a TEM instrument. **Figure 3.27** shows an image of a mesoporous CoTiO_3 monolith obtained using the STEM.

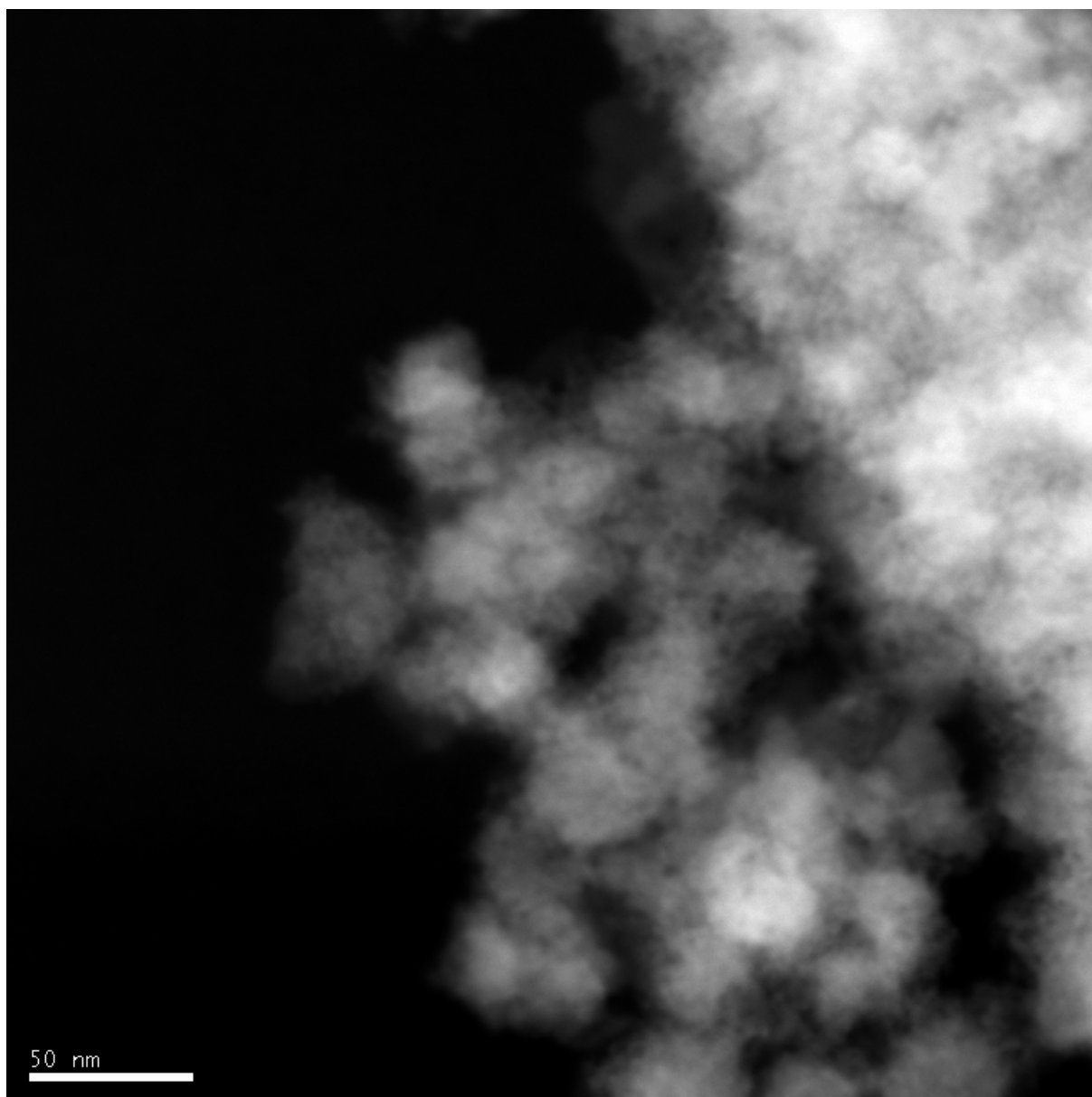


Figure 3.27 STEM image of mesoporous CoTiO_3

It should be noticed that STEM offers a better contrast compared to SEM. Therefore the “sponge-like” mesostructure is more perceivable in **Figure 3.27** compared to the SEM image in **Figure 3.26**. Another helpful characterization to be able to visualize the microstructure is the elemental mapping analysis via EDX, in the STEM mode. **Figure 3.28** shows the elemental map showing the cobalt, titanium and oxygen distribution in a piece of a mesoporous CoTiO_3 film scraped from the substrate.

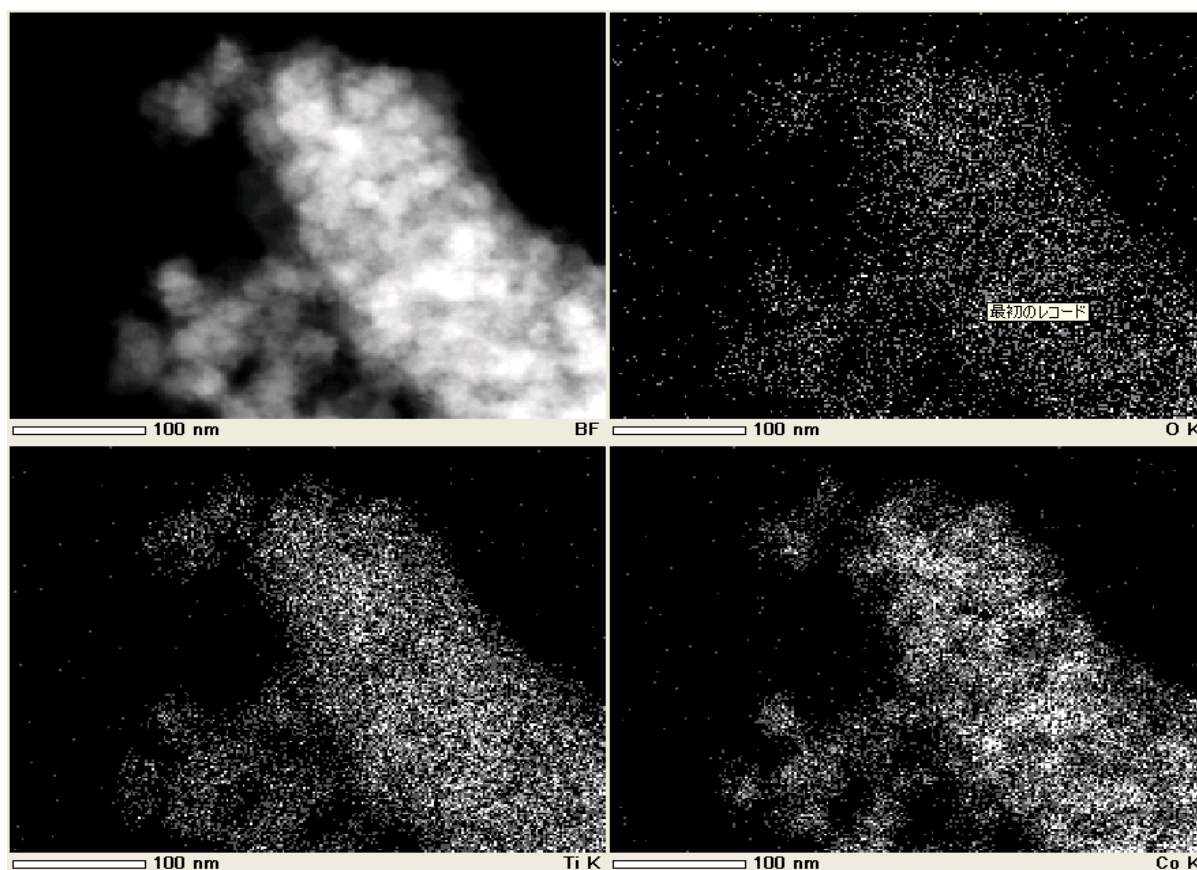


Figure 3.28 Elemental map of mesoporous CoTiO_3 (upper-left: the original image, upper-right: distribution of oxygen, down-left: distribution of titanium and down-right: distribution of cobalt.)

In general, all the elements look quite homogeneously distributed throughout the film. However, although being homogeneously distributed in large scale, it has been observed that cobalt is particularly bunched in some regions with size no more than 10-20 nm. This is attributed to the small Co_3O_4 crystal domains embedded in the CoTiO_3 matrix. Further magnification is needed to totally characterize the mesostructure of CoTiO_3 , which will be possible by using TEM.

3.3.3.3. TEM and ED

TEM has been employed in order to trace the Co_3O_4 formation in the mesoporous CoTiO_3 thin films. **Figure 3.29** and **Figure 3.30** shows the TEM images at different magnifications of a mesoporous CoTiO_3 sample prepared using 4:4:1 Co:Ti: $\text{C}_{12}\text{EO}_{10}$ mole ratio and fast calcined at 350 °C.

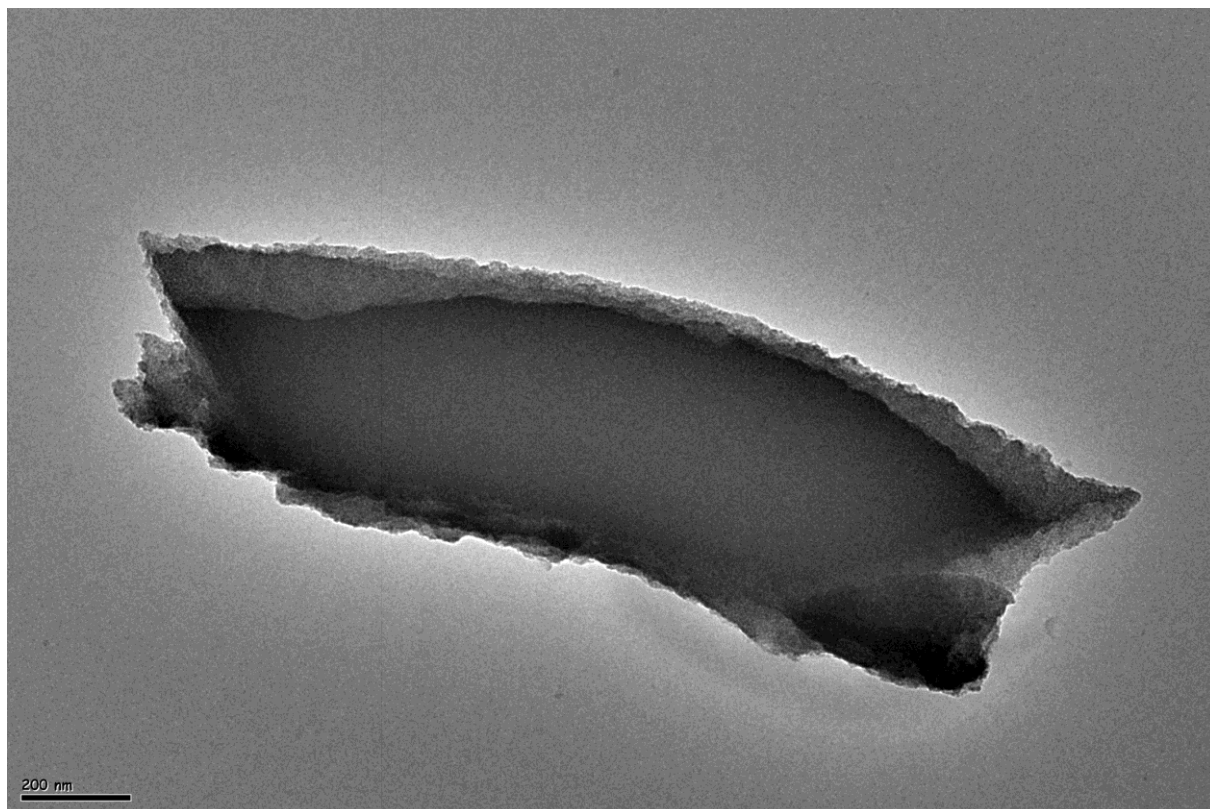
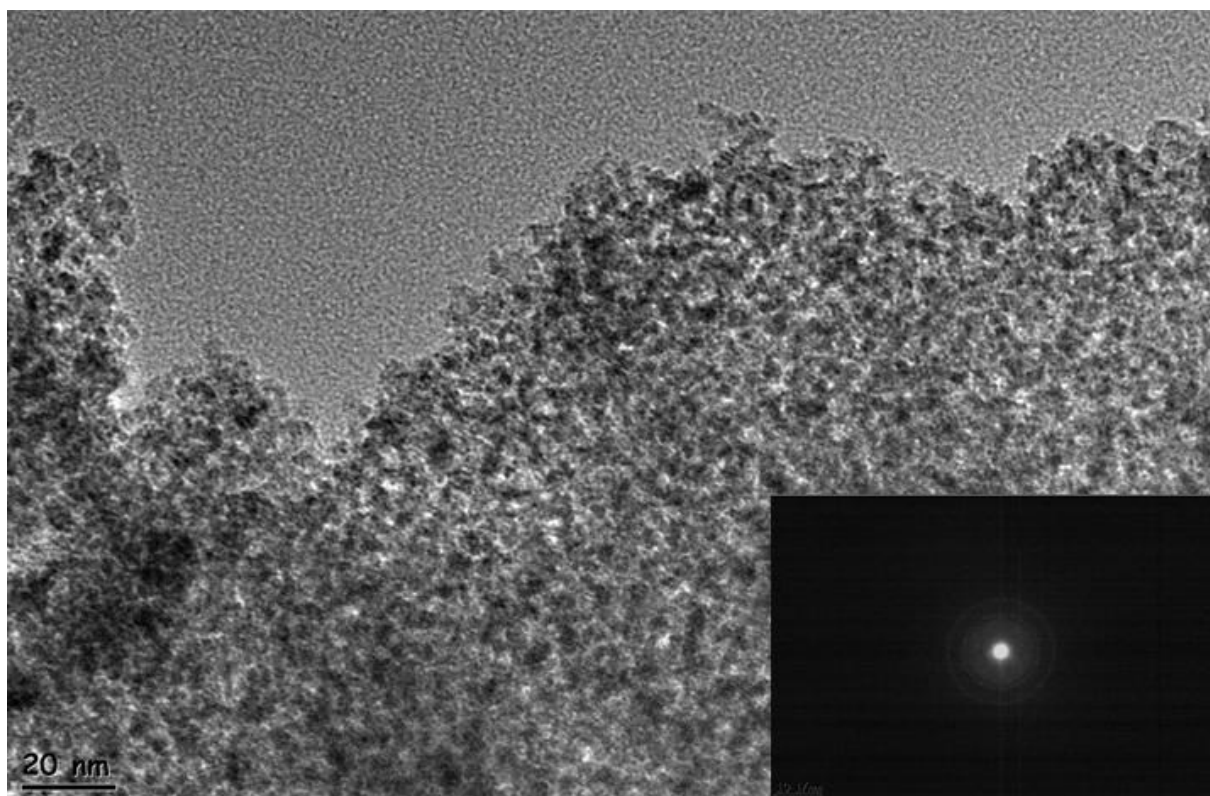


Figure 3.29 TEM image of a mesoporous CoTiO_3 film prepared using 4:4:1 Co:Ti: $\text{C}_{12}\text{EO}_{10}$ mole ratio, scraped from the substrate.

Consistent with the SEM and STEM images, the structure exhibits good homogeneity and “sponge-like” structure throughout the film. **Figure 3.30** is a high magnification TEM image focused on a smaller part of the same piece observed in **Figure 3.29**. There is also an ED pattern on the down-right corner of the image shown in **Figure 3.30**. The ED pattern shows that the mesoporous CoTiO_3 thin film prepared using 4:4:1 Co:Ti: $\text{C}_{12}\text{EO}_{10}$ mole ratio exhibits very low crystallinity. This shows that no highly crystalline bulk Co_3O_4 domains exist in the sample. In this magnification, also, no lattice fringes corresponding to Co_3O_4 have been observed. From this point of view, the as-observed cobalt bunches in elemental mapping, might be attributed to some Co-rich titanate domains or simply, amorphous Co_3O_4 .



(b)

Figure 3.30 TEM image of mesoporous CoTiO_3 thin film prepared using 4:4:1 Co:Ti: $\text{C}_{12}\text{EO}_{10}$ mole ratio recorded higher magnification (with ED pattern on the down-right corner).

Another sample with compositional mole ratio of 7:7:1 Co:Ti: $\text{C}_{12}\text{EO}_{10}$, has been prepared with the same fast calcination route. It has been already shown that Co_3O_4 population increases upon the increase of salt:surfactant mole ratio. Bulk salt crystals had appeared in the XRD patterns in the sample initially prepared with high amount of salt (see **section 3.2**). Those Co(II) salt crystals oxidize during calcination and forms Co_3O_4 crystals on top of the film. In **Figure 3.31**, a TEM image of the sample prepared using 7:7:1 Co:Ti: $\text{C}_{12}\text{EO}_{10}$ mole ratio is shown.

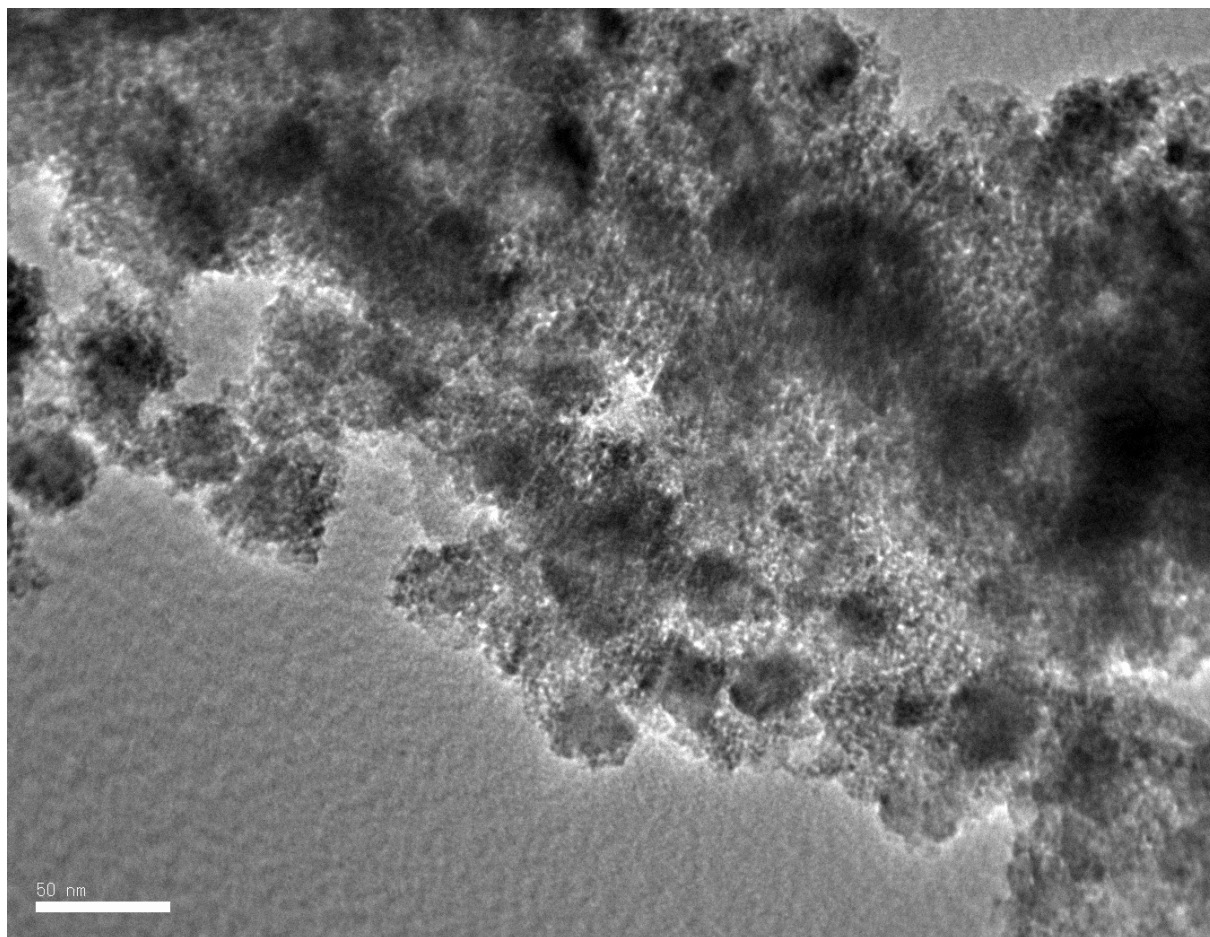


Figure 3.31 TEM image of a mesoporous CoTiO_3 monolith prepared using 7:7:1 Co:Ti:C₁₂EO₁₀ mole ratio.

In the large scaled TEM image (**Figure 3.31**), some dark spots with ~ 30 nm in size are visible. Those are possibly the Co(II) originated Co_3O_4 crystals, looking clearly different from the Co-rich regions in the previous micrographs. A closer look to the sample in **Figure 3.32** reveals the crystalline Co_3O_4 domains. On the other hand, one might not be sure about the stoichiometry of these crystals because no quantitative analysis has been made. However, Raman spectra shown earlier are signaling the existence of Co_3O_4 .

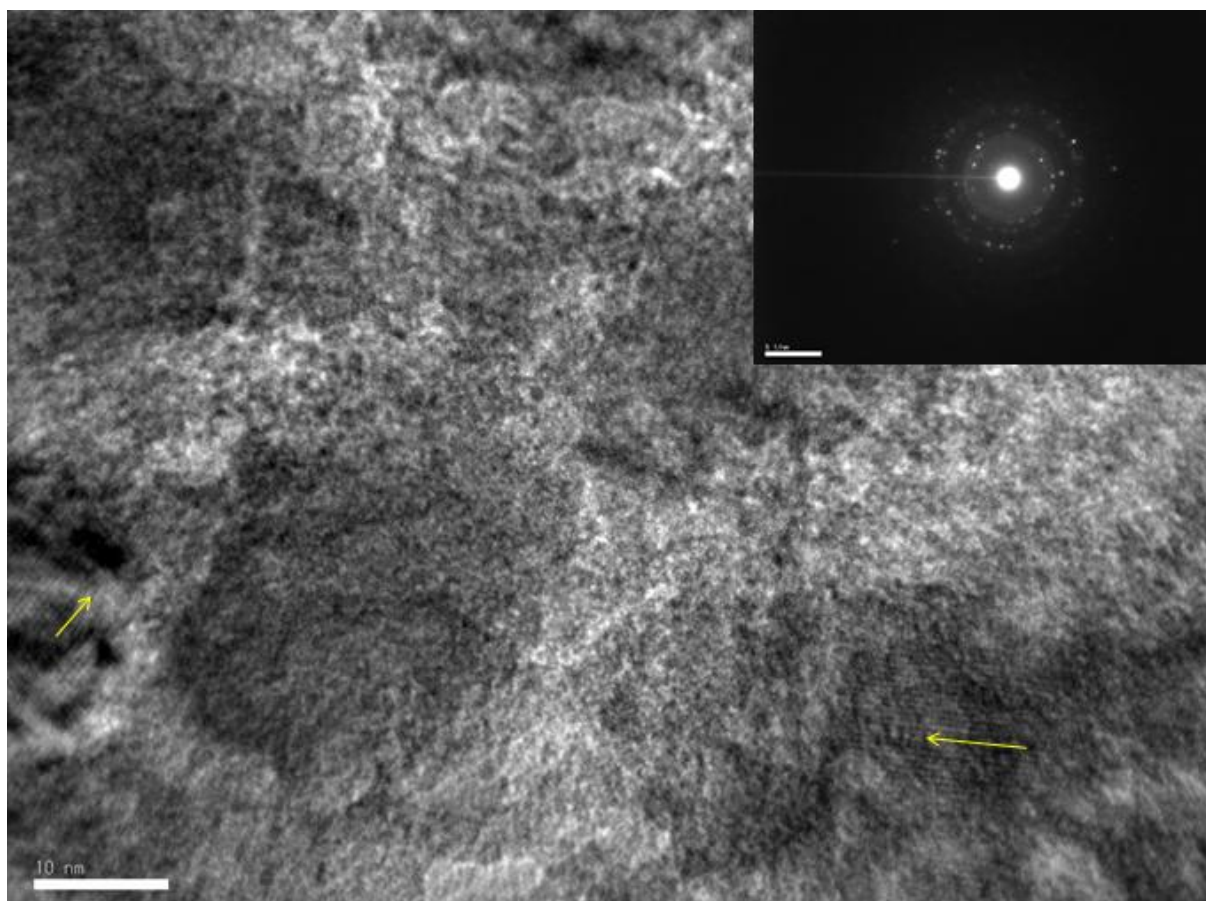


Figure 3.32 Crystalline Co_3O_4 domains in mesoporous CoTiO_3 thin film prepared using 7:7:1 Co:Ti: $\text{C}_{12}\text{EO}_{10}$ mole ratio.

In **Figure 3.32**, the lattice fringes -indicated by yellow arrows- clearly show that there are crystal structures in the sample which might be attributed to the Co_3O_4 domains. It is observed from the ED pattern, also shown on the upper-right corner of the TEM image, that there is crystalline order in the sample. Also the crystallinity is found to be higher than the sample prepared with 4:4:1 Co:Ti: $\text{C}_{12}\text{EO}_{10}$ mole ratio, because the diffraction spots are brighter when compared to the one in **Figure 3.30**.

3.3.3.4. XRD Analysis of the Co_3O_4 crystals in mesoporous CoTiO_3

Cobalt commonly exists in two oxidation states (Co(II) and Co(III)) and it forms various oxides such as CoO , Co_2O_3 , and Co_3O_4 , depending on the reaction conditions. The oxide, which is formed on top the CoTiO_3 films are found to be Co_3O_4 using Raman spectroscopy. In order to verify this, XRD pattern of a sample known to have large population of Co_3O_4 nanocrystals has been collected. The sample has been specifically prepared with high amount of salt (7:7:1 Co:Ti: $\text{C}_{12}\text{EO}_{10}$ ratio) and the spin coating has been done at 750 rpm in order to

obtain a thicker film for a better XRD measurement. The sample has been left ageing at room conditions for several hours in order to increase the salt leach out. After obtaining a dark violet colored opaque film, a sign of the complex formation between Co(II) and water, the sample has been calcined at 350 °C for 15 minutes and XRD pattern has been collected (**Figure 3.33**).

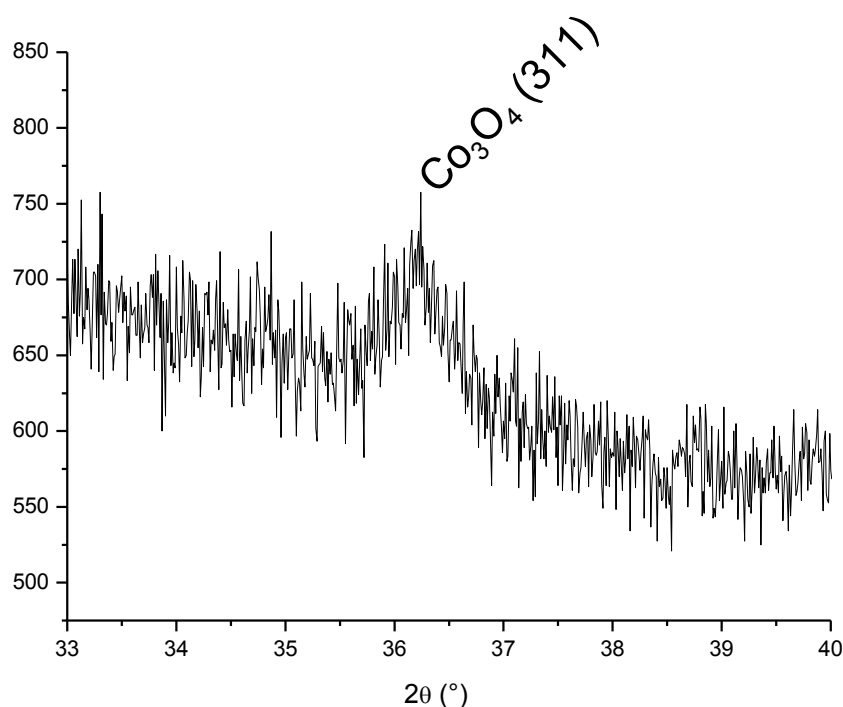


Figure 3.33 XRD pattern (between 33°-40°) of the film sample containing Co₃O₄ crystals in great quantities.

If not equipped with special apparatus, conventional XRD instruments are designed to collect data from powders and they are not sensitive to thin films. However, if the film is thick enough and the scanning rate is set to its lowest, it is possible to obtain meaningful data from our diffractometer. In this case, because the film was very thick and the scanning rate was set to 0.1 °/min; it has been possible to observe a peak around 36.3° which is attributed to the most intense diffraction line corresponding to the (311) plane of the cubic spinel phase of Co₃O₄ (ICDD PDF card #00-009-0418) The phase information about the Co₃O₄ crystals has been double-checked by both Raman spectroscopy and XRD. On the other hand, no XRD data could be obtained for CoTiO₃ because it was in an amorphous or a semi-amorphous phase. It has already been shown from the electron diffraction patterns that CoTiO₃ is not in a totally amorphous phase but yet, not in a totally crystalline phase either.

3.4. Control of Crystallinity and Pore Size of Mesoporous CoTiO₃, MnTiO₃ and Li₄Ti₅O₁₂ Thin Films via Post-Calcination Annealing

In the previous sections, the optimization processes held during the synthesis of mesoporous CoTiO₃ thin films have been explained extensively. Notice that; the salt:surfactant mole ratio and the amount of acid in the initial solution and the calcinations route of the as-prepared samples are highly effective in the LLC phase stability and the final product obtained after synthesis. Among the three materials which are in the scope of this study, CoTiO₃ was chosen for explaining in details in the synthesis and the optimizations. Because the nature of the nitrate salts are in general similar, and the only differing parameter is the metal nitrate salt in the syntheses, in this report, no further optimization studies have been done for the mesoporous MnTiO₃ and Li₄Ti₅O₁₂.

In this section, the main focus will be on the final products (i.e. monolithic powders obtained from spray coated and calcined films), and their response to thermal treatment in terms of pore size enlargement and crystallinity enhancement.

A mesoporous material with a homogeneously distributed and beforehand decided pore size is the state-of-art tailored material desired in any application. Previous works have been demonstrated in the introduction section (see **section 1.6**) regarding the pore size control of porous materials. It should be noticed that controlling the pore size and the crystallinity of mesoporous metal oxides or, in particular, mesoporous metal titanates is a delicate work which is not easy to achieve.

In this work, mesoporous CoTiO₃, MnTiO₃ and Li₄Ti₅O₁₂ monolithic powders were synthesized via MASA process using the general route for sample preparation. The solutions were spray coated on many glass substrates in order to obtain thicker films. All three materials were calcined at 350 °C for 30 min and monolithic powders (weighing around 150 ~ 200 mg) were obtained by scraping the substrates. Raman spectroscopy, XRD and N₂ sorption were employed in order to characterize the chemical, physical and crystallographic structure of the materials. The powders were subjected to several heat treatments such as, annealing at 400, 450, 500 and 550 °C for 2 hrs at each temperature. All the characterizations mentioned above for the calcined powders at 350 °C have been done after each annealing step in order to observe the effect of thermal energy on the chemical structure and mesoporosity of the materials.

3.4.1. Temperature Dependent XRD Measurements

A series of XRD measurements have been done for the three mesoporous metal titanate monolithic powders in order to track the crystallinity of the pore walls. **Figure 3.34** shows the XRD patterns of CoTiO_3 recorded upon calcination at 350 °C and after the last annealing step at 550 °C.

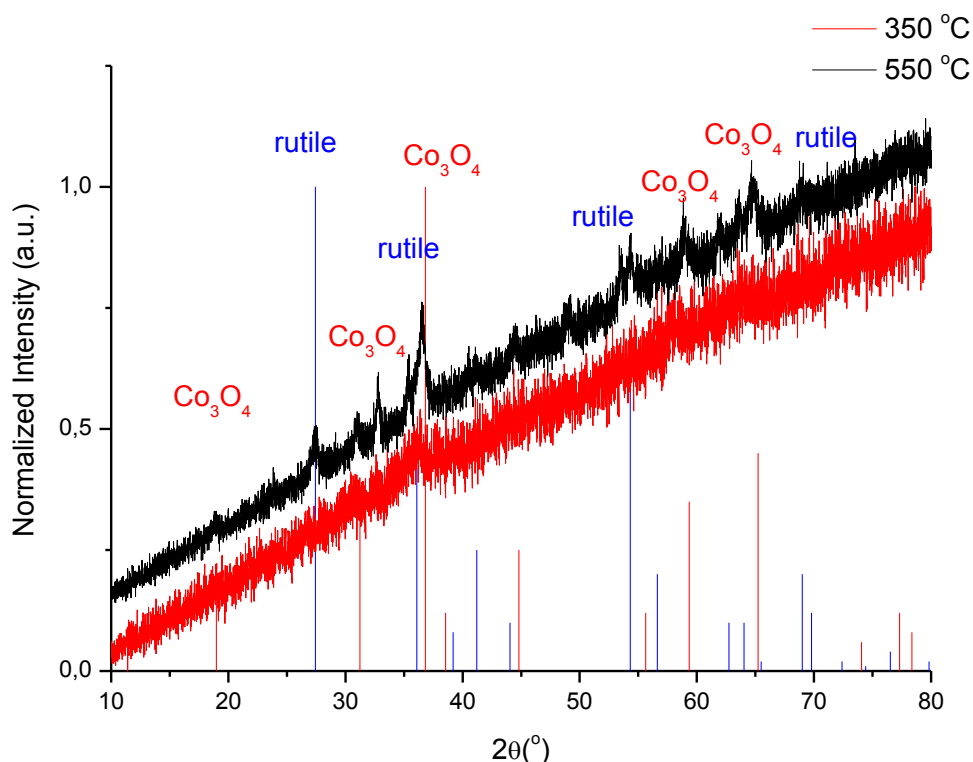


Figure 3.34. Temperature dependent XRD of mesoporous CoTiO_3 .

The XRD patterns in **Figure 3.34**, show that the material starts from an amorphous state at 350 °C and crystallizes upon further heating up to 550 °C. The intermediate temperatures such as 400, 450 and 500 °C are not shown in **Figure 3.34**, because the material exhibited amorphous properties at these three annealing temperatures. However, some small peaks become distinguishable in the pattern which belongs to sample annealed at 550 °C. In contrast to the expected crystallization of CoTiO_3 , a phase separation of CoTiO_3 to Co_3O_4 and TiO_2 has been noticed. The XRD lines observed in the pattern are attributed to a mixture of crystallized cubic spinel Co_3O_4 (ICDD PDF #00-009-0418) and rutile TiO_2 (ICDD PDF #00-021-1276). This shows that, at 550 °C, not only a phase separation but also crystallization occurs in the sample. From this point, it can be argued that the mesoporous structure is stable

up to 500 °C but the network collapses around 550 °C to form bulk crystals, detectable by XRD. It is seen from **Figure 3.35** that the MnTiO_3 exhibits similar behaviour.

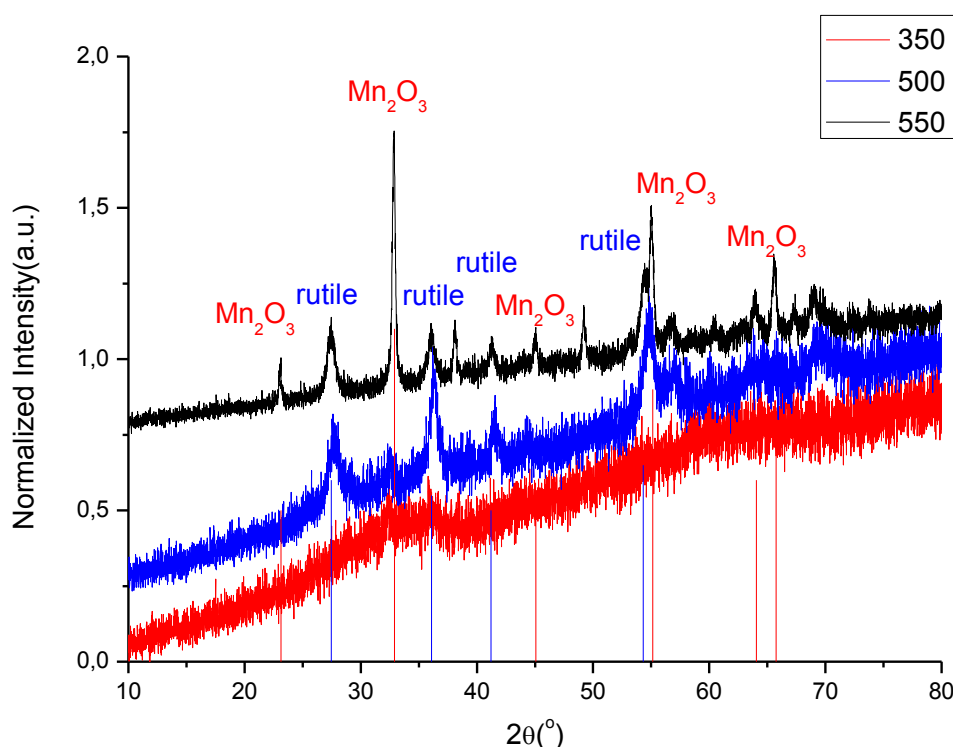


Figure 3.35. Temperature dependent XRD of MnTiO_3

Similar to the CoTiO_3 , the MnTiO_3 is also XRD amorphous at the calcination temperature. The phase separation and crystallization start at 500 °C and continue further at 550 °C. The amorphous MnTiO_3 decomposes into crystalline Mn_2O_3 (ICDD PDF #00-010-0069) and rutile TiO_2 , where the mesoporous structure is probably collapsed. However, the slight difference between CoTiO_3 and MnTiO_3 is that the crystallization of TiO_2 in MnTiO_3 starts first at around 500 °C and later accompanied by the crystallization of Mn_2O_3 at 550 °C. The XRD lines attributed to the rutile TiO_2 visible in the pattern which belongs to the sample annealed at 500 °C, indicate that the crystallization of titania is in its initial state because of the broadness of the peaks, which is well-known evidence for small nanocrystallites, calculated using Scherer's equation [75]. The XRD data of the intermediate annealing temperature are not shown because the material exhibited amorphous properties at these three annealing steps, just as in the CoTiO_3 case.

Another interesting aspect about the XRD patterns of both CoTiO_3 and MnTiO_3 is that, the patterns are unusually slopped. This effect is explained by the increasing x-ray self-emission

of the samples upon x-ray irradiation. This is due to the closeness between the energies of Cu- $K\alpha$ -coming from the x-ray source- and the core shells of Co and Mn. The data is kept untouched without any correction or manipulation in order to maintain the original XRD pattern and make accurate comments. This behaviour of the CoTiO_3 and MnTiO_3 makes it difficult to measure the XRD pattern. It is likely that due to self-absorption of x-ray by the sample makes x-ray to diffuse not too much into the sample to collect reasonable XRD patterns. However, there is no such issues in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and reasonable XRD patterns were collected from those samples, see section below.

Figure 3.36 shows the XRD patterns of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ calcined at 350 °C and annealed at different temperatures.

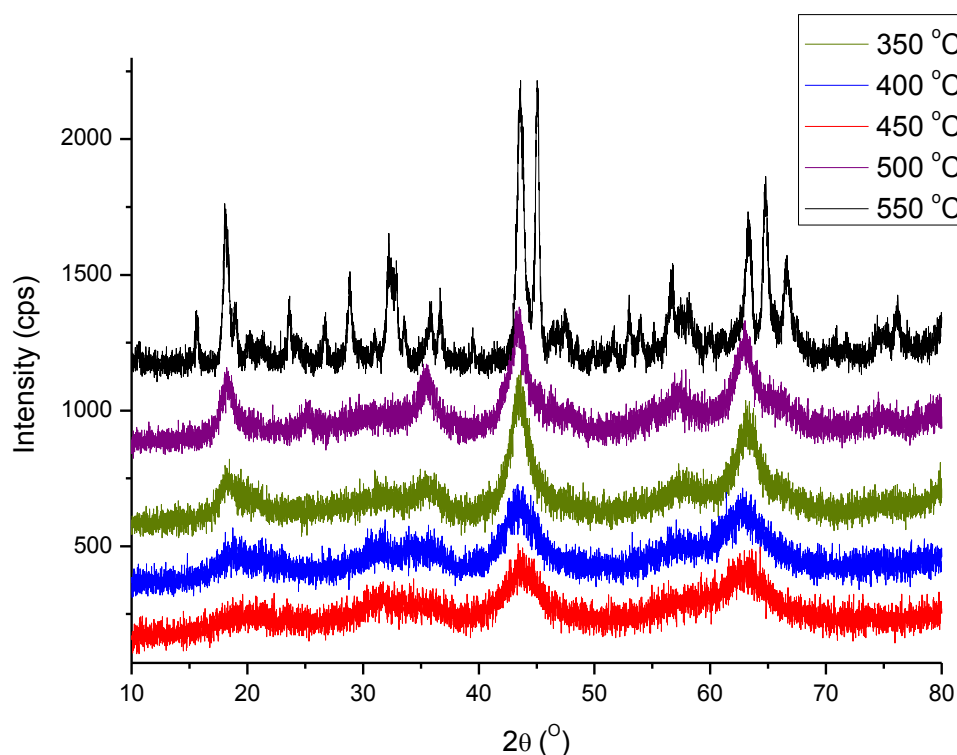


Figure 3.36. Temperature dependent XRD patterns of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Unlike CoTiO_3 and MnTiO_3 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is not amorphous even at 350 °C. The broad diffraction lines, proving that there are small crystallites in the material, show that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibits nanocrystalline structure even at low temperatures (compared with ICDD PDF #00 049 0207 of crystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$). **Figure 3.36** contains all the XRD information about all the temperature range from 350 to 550 °C. As expected, the diffraction lines are getting sharper upon further annealing at higher temperature. The patterns, which belong to the

temperatures 350, 400, 450 and 500 °C indicate that a single phase is formed in the material and the crystallinity is enhanced in favor of the initially formed phase. Furthermore, no other sharp peaks attributed to a secondary phase appear in the pattern even at 500 °C. However, multiple sharp peaks appear in different locations in the pattern which belongs to the sample annealed at 550 °C. This is a clear evidence for a phase separation and structural collapse similar to CoTiO_3 and MnTiO_3 . **Figure 3.37** shows the same XRD patterns already given in **Figure 3.36** with only the data of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ annealed step by step up to 500 and 550 °C with some helpful peak assignments.

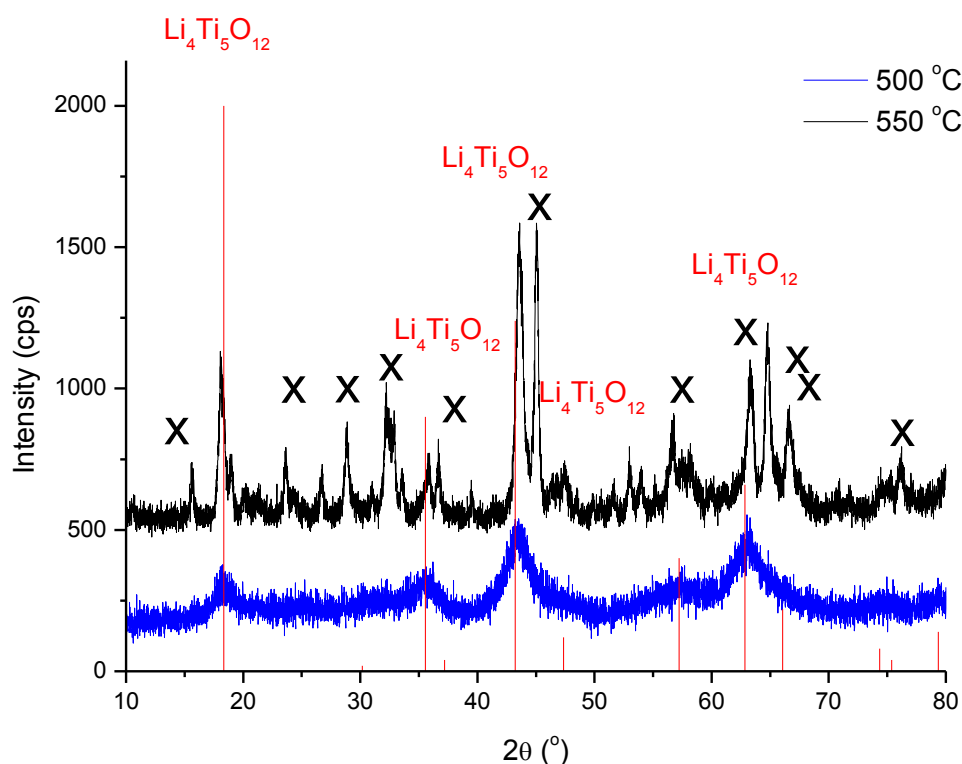


Figure 3.37 XRD pattern of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ annealed step by step up to 500 and 550 °C with phase labels

The XRD pattern, annealed step by step up to 500 °C, shows definitely an existing nanocrystalline phase of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with no bulk impurities. This statement is also valid for all annealing step lower than 500 °C. However, multiple peaks denoted by X appearing in the XRD pattern which belongs to the sample annealed step by step up to 550 °C, cannot be attributed to the known phases of lithium titanate compounds or polymorphs of TiO_2 . A new compound with stoichiometry close to $\text{Li}_4\text{Ti}_5\text{O}_{12}$, but lacking slightly in Ti(IV), might be formed and crystallized upon further heating. On the other hand, it is understandable that in proportion with the lack of Ti(IV) in the newly formed $\text{Li}_x\text{Ti}_y\text{O}_z$ compound.

3.4.2. Temperature Dependent Raman Spectroscopy

Raman spectroscopy is a fast and powerful technique to characterize phases in the sample. The beauty of Raman spectroscopy over XRD is that, it requires very small amount of sample (usually less than 1 mg) and due to the higher sensitivity to atomic bonds, any crystal formation can be detected even from the thin film samples which are believed to be amorphous according to XRD results. In this sense, XRD measurements should always be coupled with Raman spectroscopy, especially in puzzling circumstances, like in the case of this study.

A series of Raman spectra has been collected from the same samples used in XRD characterization. **Figure 3.38** shows the Raman spectra of CoTiO_3 prepared, calcined and further annealed at higher temperatures as explained in the previous section.

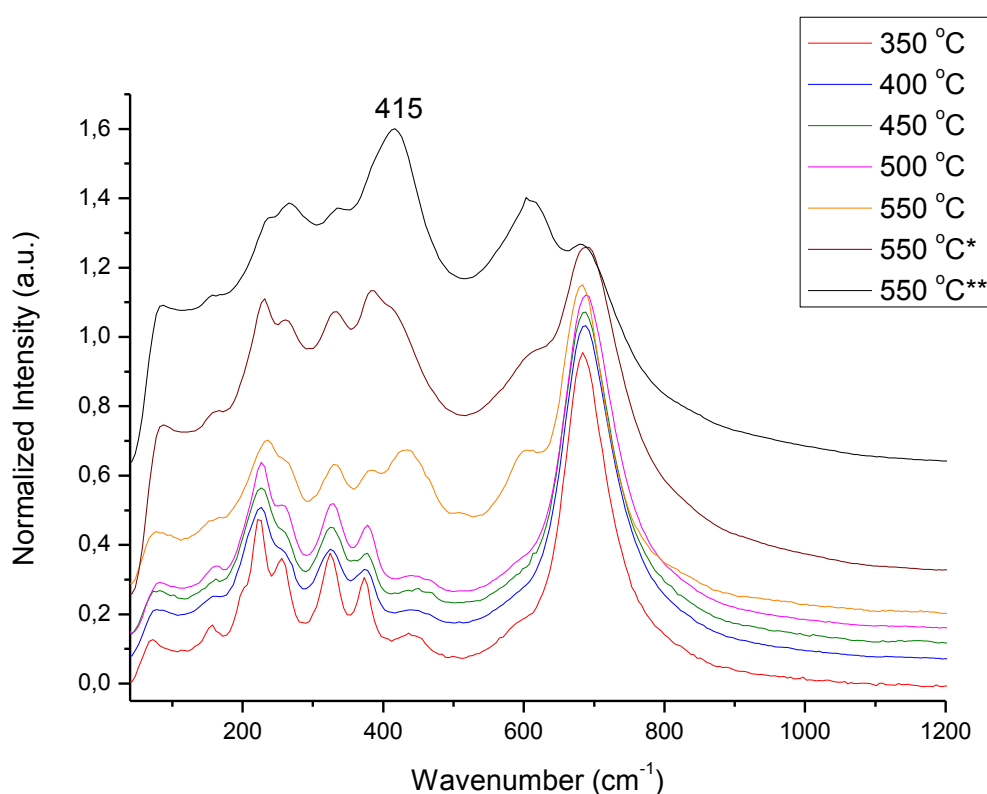


Figure 3.38 Temperature dependent Raman Spectra of CoTiO_3 .

Expectedly, Raman spectra of CoTiO_3 contain far more information than XRD patterns. The Raman spectra of the sample annealed step by step up to 500 °C and below show seven peaks at 156, 224, 258, 328, 377, 443, and 684 cm^{-1} which are attributed to the ilmenite phase of

CoTiO₃. [74] As per the theoretical analysis, 10 Raman modes (5A_g + 5E_g) were expected for the ilmenite structure of CoTiO₃. [76] Some of the peaks are shadowed from other broad peaks. This is due to the nanocrystalline nature of the material where the crystal size is so small and notice that, no peaks had been observed in XRD patterns. However, consistent Raman spectra show that the material has pore walls exhibiting low crystallinity but yet, the crystals are in a singular ilmenite phase of CoTiO₃ and this structure is stable up to 500 °C. On the other hand, new phases reveals when mesoporous CoTiO₃ is stepwise annealed up to 550 °C. Three spectra labeled as 550 °C, 550 °C* and 550 °C** in the legend, are shown for the annealing step of 550 °C and they are all different from each other. Actually, they represent the spectra collected from the same spot of the same sample with different Raman laser irradiation time. The first spectrum labeled as 550 °C is the initially collected spectrum, the second -which is labeled as 550 °C*- is collected after 5 minutes and the third -which is labeled as 550 °C**- is collected after 10 minutes of Raman laser irradiation. The interesting story behind this phenomenon is that, an obvious phase separation occurs under the Raman laser irradiation. Varadwaj *et al.* showed that such degradation is possible for metal oxide nanomaterials under Raman laser irradiation. [77]. In this case, a formation of nanocrystalline rutile phase of TiO₂ is in evidence due to the peaks observed at 267, 415 and 610 cm⁻¹. The most intense peak around 415 cm⁻¹ appearing in the spectrum is attributed to the red-shifted E_g mode of rutile TiO₂ having a theoretical value of 440 cm⁻¹. [78] The reason of this red-shift is well explained in literature as the vacancies of oxygen in TiO_(2-x) nanostructures. [79] The oxygen deficiency in the initially formed rutile phase of TiO₂ is meaningful because the oxygen number in the stoichiometric CoTiO₃ is not enough to form Co₃O₄ and TiO₂. For that reason, the formation of stoichiometric rutile requires extra energy which will be provided from the Raman laser and extra oxygen which will be provided from the air. In order to prove this, another experiment under the Raman laser is held using the same sample, which exhibited the phase separation due to the annealing at 550 °C. The sample is kept under the open laser of the Raman spectroscopy for a certain time and several Raman spectra are collected at different points (**Figure 3.39**).

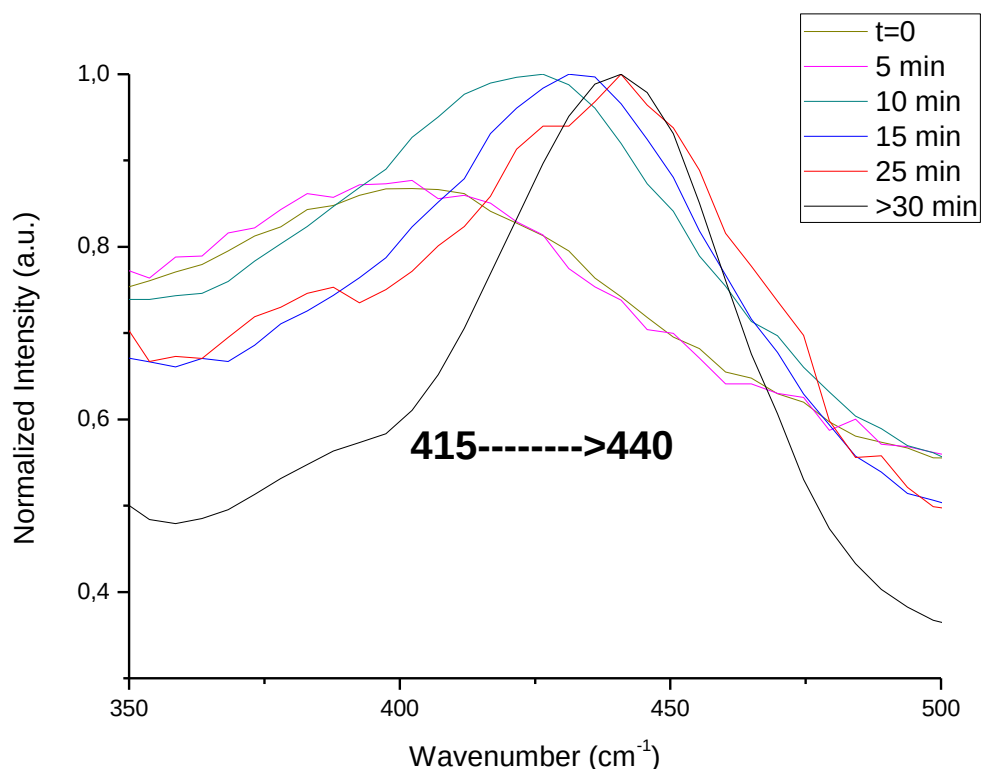


Figure 3.39 Evidence of the stoichiometric rutile formation upon phase separation in mesoporous CoTiO_3 under the laser of the Raman spectrophotometer.

It is observed from the Raman spectra, shown in **Figure 3.39**, that after 10 min of laser irradiation, a significant blue shift start to take action. This blue shift shows that the value of x in TiO_{2-x} is getting smaller as the enough time and energy for oxide formation is provided and the structure is becoming more like regular crystalline rutile phase of TiO_2 . It should also be noticed that after 25 min of irradiation, the value sets to its theoretical wavenumber of 440 cm^{-1} and upon further irradiation, blue shift is no longer observed. Instead of shifting, the peak stays stable at 440 cm^{-1} and it starts to get sharper, which is also an indication of enhanced crystallinity. This phenomenon itself, points to the clear evidence that the material is highly reactive, owing to its mesoporous nature and, even a low-power laser can create a local solid state reaction.

The Raman spectroscopy results about the existing CoTiO_3 phase and its separation to newer phases such as Co_3O_4 and rutile TiO_{2-x} (and later on, TiO_2) are in a good agreement with the XRD results and not to mention, the insights they provided in understanding the crystallographic nature of the mesoporous CoTiO_3 are quite enlightening.

A similar behavior of phase separation and rutile formation with oxygen deficiency is also observed in mesoporous MnTiO_3 as well. **Figure 3.40** shows the temperature dependent Raman spectra of MnTiO_3 .

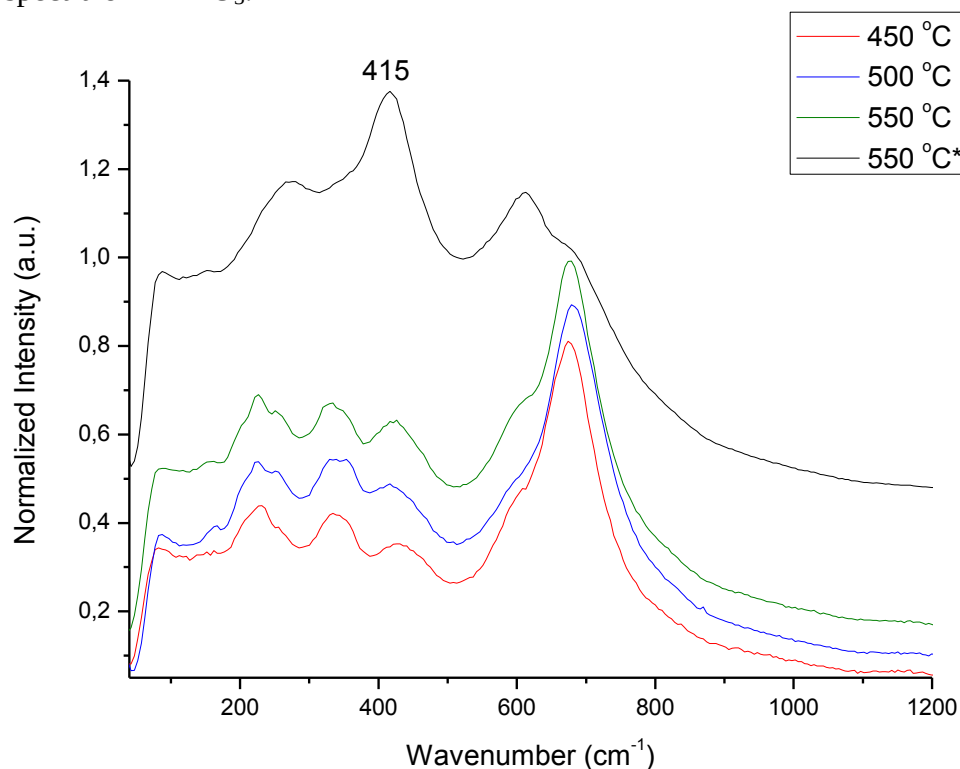


Figure 3.40 Temperature dependent Raman spectra of MnTiO_3 .

The spectra clearly display characteristic MnTiO_3 peaks [80] at 158, 206, 224, 255, 326, 352, 426, 606, and 676 cm^{-1} , between 450 and 500 $^{\circ}\text{C}$, indicating a nanocrystalline nature of the pore wall content due to the broadness of the peaks. Also, similarly to CoTiO_3 , a peak which is around 415 cm^{-1} is attributed to the newly formed rutile phase of TiO_2 rises upon further irradiation with the Raman laser.

Figure 3.41 shows the Raman spectra of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ annealed at increasing temperatures. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ related peaks [81] [82] at 658, 407 and 222 cm^{-1} appear as low as 350 $^{\circ}\text{C}$ and intensify by increasing the annealing temperature up to 500 $^{\circ}\text{C}$. However, as an indication to a phase change, new peaks start emerging at around 550 $^{\circ}\text{C}$. The peak at 658 cm^{-1} completely shifts to 633 cm^{-1} and a new shoulder appears at 480 cm^{-1} and the peak at 221 cm^{-1} shift or splits into two new peaks at 197 and 272 cm^{-1} . Two new peaks grow in intensity by annealing at higher temperatures at 809 and 922 cm^{-1} , characteristic for surface peroxy species. These observations are consistent with the changes observed in the XRD patterns. The origin of these changes is attributed to crystallization of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and phase change/separation at

higher temperatures. The phase separation leads a new unidentified $\text{Li}_x\text{Ti}_y\text{O}_z$, because the new peaks do not belong to any phase of pure titania.

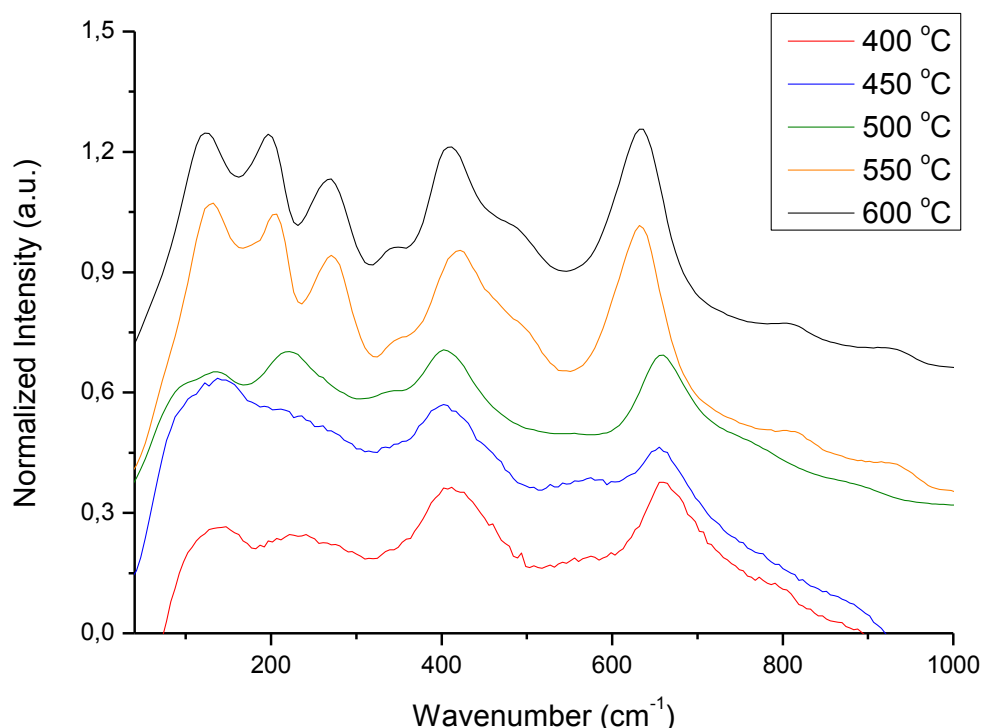


Figure 3.41 Temperature dependent Raman spectra of $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Apparently, all three mesoporous metal titanates start from a nanocrystalline structure with the targeted phase at low temperatures and consistent with the XRD data, phase separation/transition occurs at around 550 °C.

3.4.3. Temperature Dependent N_2 Sorption Measurements and Pore Size Control of Mesoporous Metal Titanates

So far, the chemical and structural characterization of mesoporous CoTiO_3 , MnTiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ monolithic powders and their response to thermal treatment have been studied using XRD and Raman spectroscopy in the previous two sections. However, no matter how valuable those results were, they did not give any information about the mesoporosity of these materials. Only some speculations on the crystal size of the materials were deducted from the broadness of the peaks in the XRD patterns and Raman spectra. On the other hand, N_2

sorption technique is the most accurate method for the characterization of any porosity in materials.

In order to determine the specific surface area and the pore size distribution of the mesoporous CoTiO_3 , MnTiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ monolithic powders and their responses to thermal treatment, N_2 sorption technique is employed. Full isotherms constituting of N_2 adsorption and desorption points are collected at 77 K (in liquid nitrogen), first 5 adsorption points are used for BET surface area calculations and all desorption points are used for BJH desorption cumulative pore volume (pore size distribution) calculations. The same samples used in XRD and Raman spectroscopy are also used in N_2 sorption measurements and an isotherm is collected at each annealing step of each material described earlier. **Figure 3.42** shows the set of isotherms of CoTiO_3 collected from each annealing step.

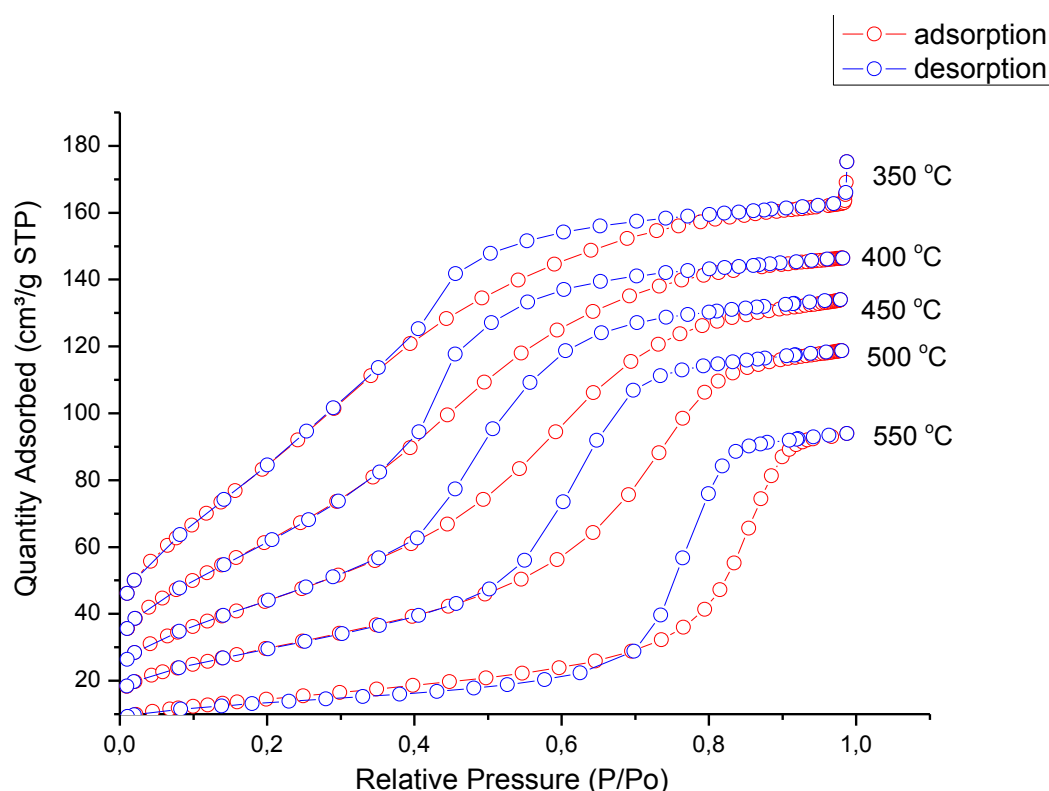


Figure 3.42 Temperature dependent isotherms of mesoporous CoTiO_3

All five N_2 sorption isotherms shown in **Figure 3.42** are in type IV. This is a well-known evidence for mesoporous structure and shows that CoTiO_3 ($\text{Co}_3\text{O}_4 + \text{TiO}_2$, after annealing at 550 °C) is mesoporous at all temperatures. Typically, an isotherm is examined by means of its slope in the lower P/P_0 values, and by the shape and position of its hysteresis. The slope gives

an idea about the surface area; usually the higher the slope is, the higher the surface area of the material will be calculated. By brief observation, it can be seen that the decrease of the slope of the isotherms of CoTiO_3 is almost proportional to the increase of the annealing temperature. This means that the surface area of the material decreased gradually upon further annealing. At all temperatures, the size of the hysteresis did not change dramatically. This is a clue for the uniformity of the pores. However, the shift of the hysteresis to the higher P/P_0 intervals shows that the average pore size of the material changed with different annealing temperature or, to be more specific; the average pore size of the mesoporous CoTiO_3 monoliths increased in parallel with the increasing annealing temperatures without any deterioration in the uniformity of the mesoporous network. **Figure 3.43**, the pore size distribution plots at different temperatures, explains this statement better.

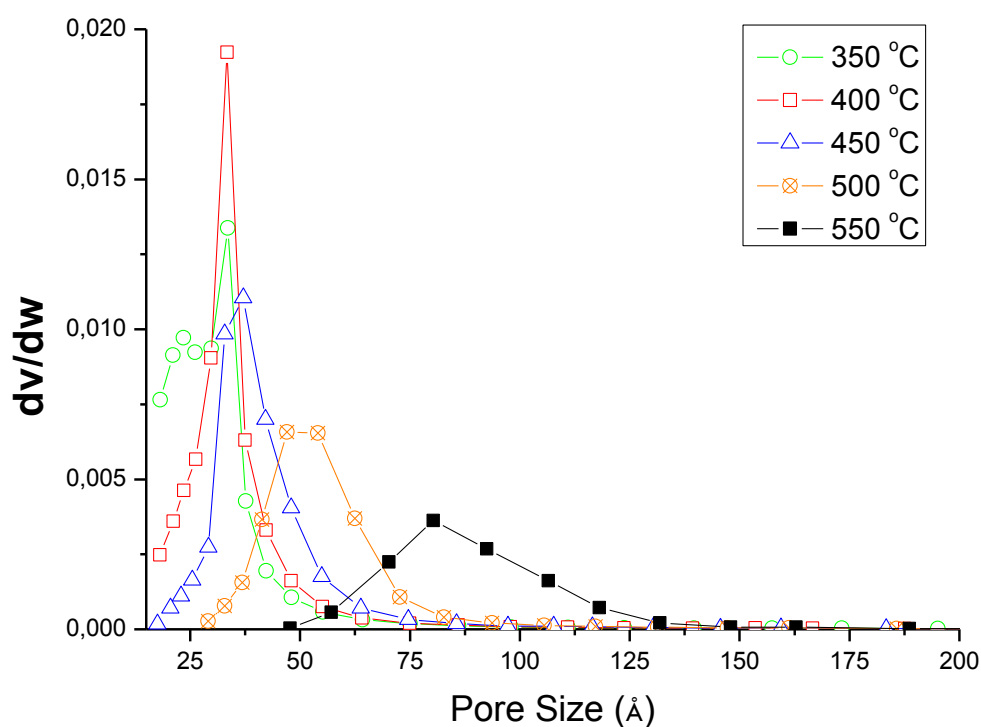


Figure 3.43 Pore size distribution plots of CoTiO_3 at different annealing temperatures.

The pore size distribution plot of a mesoporous material is the data, which shows the distribution of the volume occupied by the pores with different sizes. The sharper the plot is, obviously, will be the more homogeneous the pore size distribution. For instance, remember

from the isotherms in **Figure 3.42**, the BET surface area seemed to be higher for the sample calcined at 350 °C compared to the further annealed at 400 °C. However, the plot of the sample annealed at 400 °C has a sharper peak around 30 Å with a higher intensity than the one which belongs to the sample calcined at 350 °C. If it is analysed more carefully, there is another peak in the sample of 350 °C, in the region below 25 Å. This shows that the material possesses two different pore systems, which disappear upon further annealing. The smaller pores (~2.0 nm), nearly close to the micropore region, probably join the bigger pores (~3.0 nm) due to the sintering of the material and the volume of the original mesopore (at ~3.0 nm) seen in 400 °C intensifies. Not to mention, the pore size distribution broadens slightly at higher temperatures however, it remains uniform at all annealing temperatures. **Table 3.2** lists all the information of mesoporosity of CoTiO₃ such as BET surface area, mean pore diameter and specific pore volume calculated from the isotherms at all temperatures.

Table 3.2: Temperature dependent N₂ sorption data of mesoporous CoTiO₃ monolithic powder.

	BET Surface Area (m ² /g)	Mean Pore Size (nm)	Specific Pore Volume (cm ³ /g)
350 °C	316	3.1	0.26
400 °C	227	3.3	0.23
450 °C	161	4.0	0.21
500 °C	107	5.4	0.19
550 °C	52	8.7	0.15

On the other hand, mesoporous CoTiO₃ thin film synthesized in this study is by so far, the most attractive achievement among the previous studies. The thin films exhibit optical transparency and have a record high BET surface area of 316 m²/g. Another interesting aspect is that the material contains uniformly distributed mesopores and the pore size can be controlled via post-calcination annealing steps. Not to mention that the production method is a short time and a quite straightforward process compared to the previously shared literatures. One should also notice that the trend of the pore size growth is harmonious up to 500 °C and somehow breaks at 550 °C. This is explained by the phase separation of CoTiO₃ to Co₃O₄ and TiO₂, and by the noticeable bulk crystallization of those products, already deduced from previous XRD and Raman results. On the other hand, even the degraded product at 550 °C,

$\text{Co}_3\text{O}_4\text{-TiO}_2$ nanocomposite, can be interesting in other applications and also shows mesoporosity.

The same analysis is also done for mesoporous MnTiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ monolithic powders.

Figure 3.44 and **Figure 3.45** show the temperature dependent isotherms and the pore size distribution plots of MnTiO_3 and, **Figure 3.46** and **Figure 3.47** show the same data for $\text{Li}_4\text{Ti}_5\text{O}_{12}$, respectively.

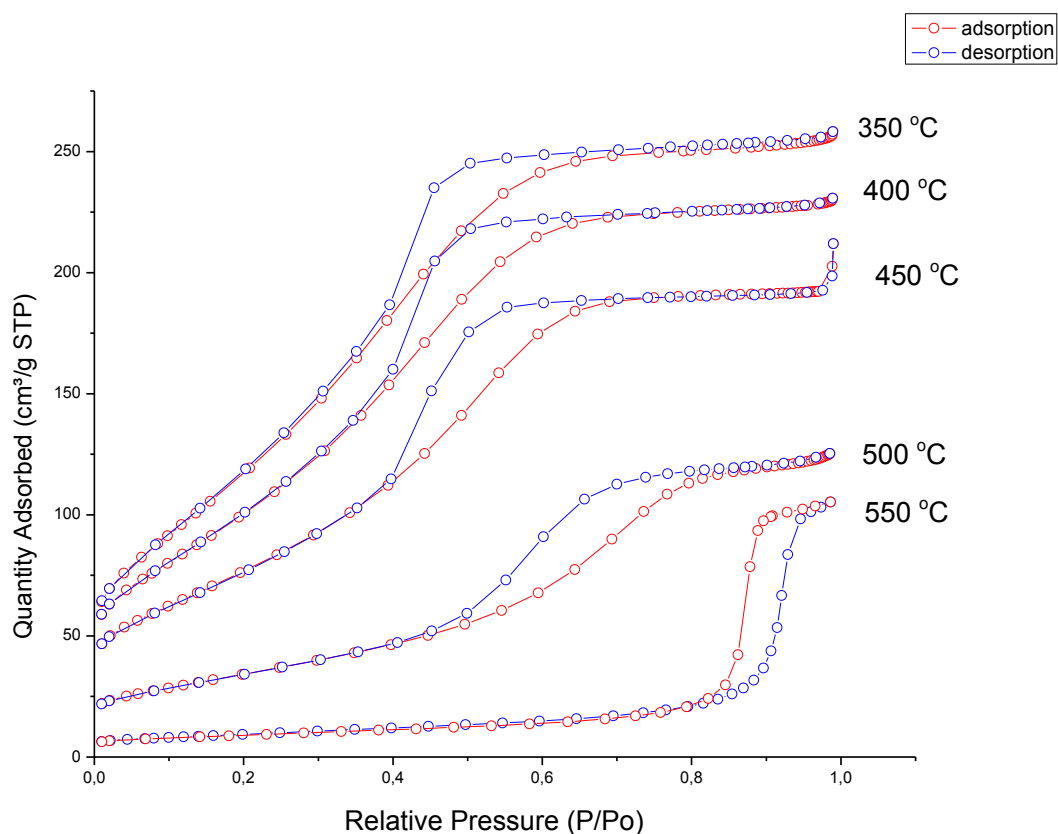


Figure 3.44 Temperature dependent isotherms of mesoporous MnTiO_3 .

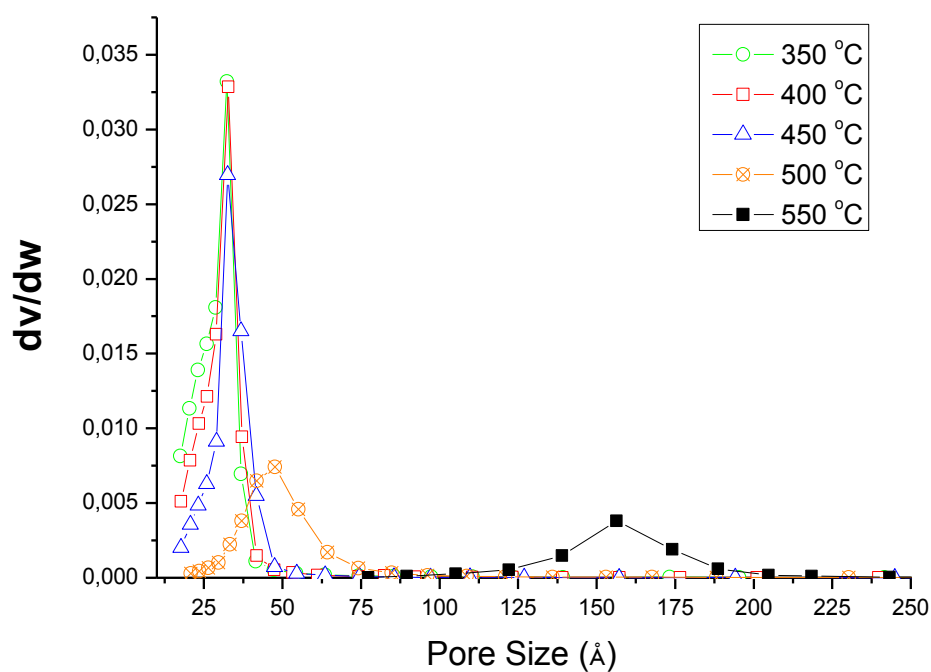


Figure 3.45 Pore size distribution plots of MnTiO_3 at different annealing temperatures.

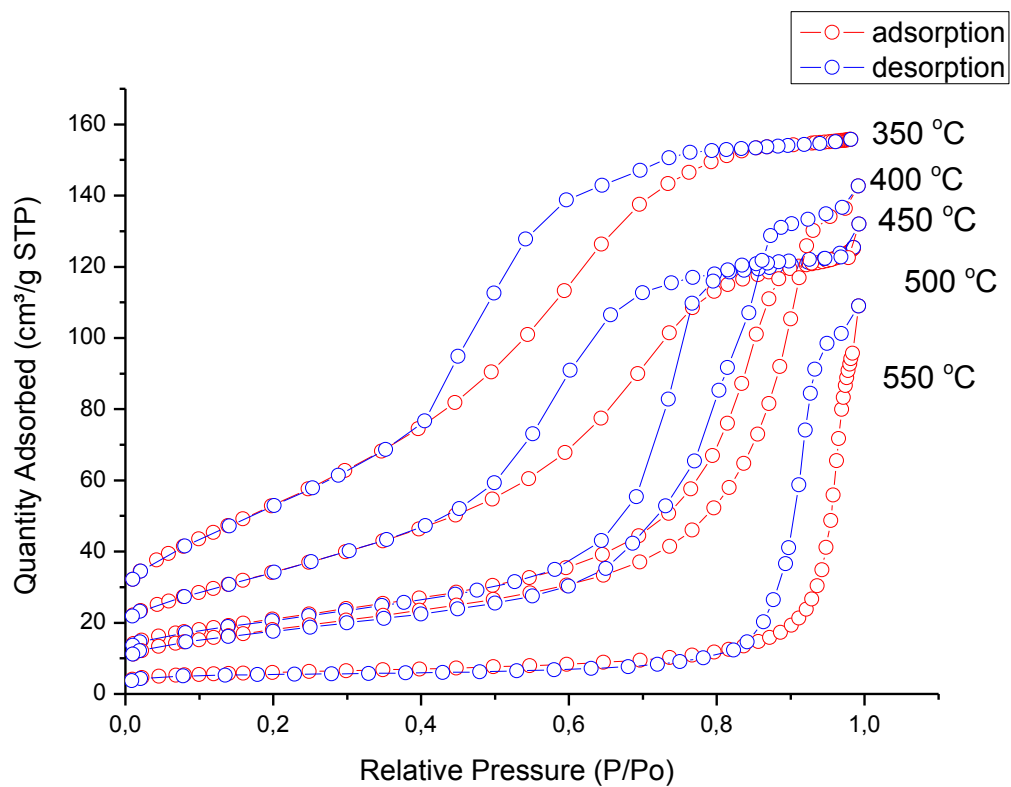


Figure 3.46 Temperature dependent isotherms of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

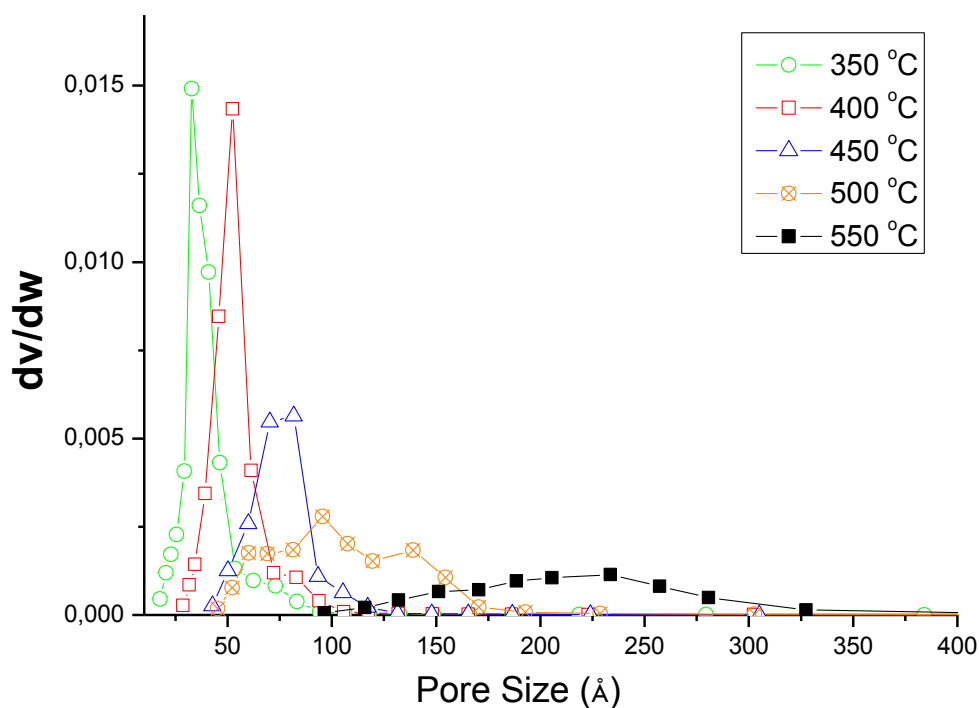


Figure 3.47 Pore size distribution plots of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at different annealing temperatures.

All the isotherms of MnTiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at all temperatures are type IV isotherms, showing that all the structures are mesoporous at all temperatures. It is seen from **Figure 3.44** that the response of the mesoporous MnTiO_3 to the thermal treatment is similar to CoTiO_3 and the slope of the isotherms decreases gradually upon annealing at higher temperatures. The shape of the hysteresis is also quite similar to each other in the isotherms which belong to the samples annealed at 350, 400 and 450 °C. This is a sign for the stability of the mesoporous network, in other words, no dramatic change occurred in terms of mesoporosity at these temperatures. Notice that such behavior was also observed in CoTiO_3 at all temperatures below 550 °C. However, in the MnTiO_3 case, the shape of the hysteresis changes remarkably at 500 °C. This might be related with the earlier crystallization of the rutile phase of TiO_2 at 500 °C, and deterioration of the mesoporous network, also deduced from the XRD patterns (see **Figure 3.35**). **Table 3.3** contains all information calculated from the isotherms of MnTiO_3 .

Table 3.3: Temperature dependent N₂ sorption data of mesoporous MnTiO₃ monolithic powder.

	BET Surface Area (m ² /g)	Mean Pore Size (nm)	Specific Pore Volume (cm ³ /g)
350 °C	445	3.1	0.40
400 °C	370	3.2	0.36
450 °C	270	3.4	0.31
500 °C	124	5.6	0.20
550 °C	33	15.6	0.16

The material presented here in this study has the potential of being a benchmark in its own category owing to its world record high BET surface area of 445 m²/g after calcination at 350 °C. In fact, 445 m²/g is quite high for any mesoporous metal oxide ever reported. Based on the extensive review paper recently published by Ferdi Schüth, a recognized scientist known to work mesoporous materials for years, and his co-worker Dong Gu; only few binary metal oxides have exceeded the BET surface area value achieved in this study. [24]

Otherwise, mesoporous MnTiO₃ exhibits similar behavior to CoTiO₃ with slight difference in pore size growth nature. Remember that CoTiO₃ started with two pores system and upon further annealing, the smaller pores disappeared to probably merge into the bigger pores. In the MnTiO₃ case, the smaller pores are less distinct, based on the shoulder (not a sharp peak) appearing in the microporous region of the pore size distribution plot in **Figure 3.45**. For that reason, it is hard to speak about a smaller secondary pore system however, the shoulder which is mentioned before, disappears completely at 450 °C. It is also seen that controlling the pore size of MnTiO₃ below 450 °C is harder than CoTiO₃ because the change in the diameter at each step is around 0.1-1.2 nm, which is in the error margin ($\pm 10\%$) of N₂ sorption measurement. However, the increasing trend from 3.1 to 3.4 nm between 350 and 450 °C is clueing in and probably, the pore size growth might be enhanced by expanding the annealing time. On the other hand, a significant growth to 5.6 and 15.6 nm is observed at annealing temperatures of 500 and 550 °C, respectively.

Beyond any doubt, due to its application in Li ion batteries, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is the most interesting and highlighting material among the three metal titanates reported here. **Table 3.4** contains all information calculated from the isotherms of $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Table 3.4: Temperature dependent N_2 sorption data of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ monolithic powder.

	BET Surface Area (m^2/g)	Mean Pore Size (nm)	Specific Pore Volume (cm^3/g)
350 °C	193	4.3	0.25
400 °C	152	5.2	0.27
450 °C	75	7.3	0.19
500 °C	65	9.9	0.21
550 °C	21	22	0.17

Mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ monoliths calcined at 350 °C have a larger BET surface area than any of its analogues reported in the literature. [65] [83] [66] [67] [84] [68] [69] Only J. Chen *et al.* reported some nest-like $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanostructures having BET surface area of 219 m^2/g . [85] However, the material is produced via a complex procedure, which takes more than 24 hrs, thus making it less efficient compared to the mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin films or monolithic powders produced via MASA synthesis within no more than 45 min. Notice that the pore walls have an average size of 4.3 nm and the material displays crystalline pore walls (see the broad peaks in the XRD pattern in **Figure 3.36**).

Another attractive aspect about the mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is the more distinctive change in the pore size compared to CoTiO_3 and MnTiO_3 upon annealing. The mesopores start from 4.3 nm and continue to grow, up to 9.9 nm almost linearly by preserving the mesoporous network and the nanocrystalline pore walls made of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Thus far, no pore size control system with such accuracy and controllability has been reported yet. Therefore, using MASA approach, one needs only to calcine the as-prepared material at 350 °C and anneal it at an appropriate temperature for 2 hrs in order to obtain a mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with a desired pore size and crystalline pore walls. For instance, at the annealing step of 500 °C, as an indication for crystal growth, the material displays sharper XRD peaks. It means that the material has larger crystallites when the BET surface area is decreased to 65 m^2/g . Despite the crystallization, the BET surface area of the material at 500 °C is still better than its many other

equals in the literature. Not to mention that the pore size distributions are quite narrow at all annealing temperatures below 500 °C.

On the other hand, a degradation which is similar to CoTiO_3 and MnTiO_3 occurs for mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as well, at 550 °C. The material transforms into an unknown $\text{Li}_x\text{Ti}_y\text{O}_z$ compound by undergoing bulk crystallization and, probably for that reason, the BET surface area falls drastically to 21 m^2/g .

3.4.4. TEM Analysis of Mesoporous Metal Titanate Thin Films

A series of TEM images have been collected for a complete characterization in regard to the synthesis of mesoporous CoTiO_3 , MnTiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin films. The images belong to the mesoporous monoliths scraped from the glass substrates, which are spin coated using a spin speed of 7000 rpm. **Figure 3.48** shows the largely scaled TEM images of CoTiO_3 monolithic thin film piece calcined at 350 °C and scraped from a glass substrate.

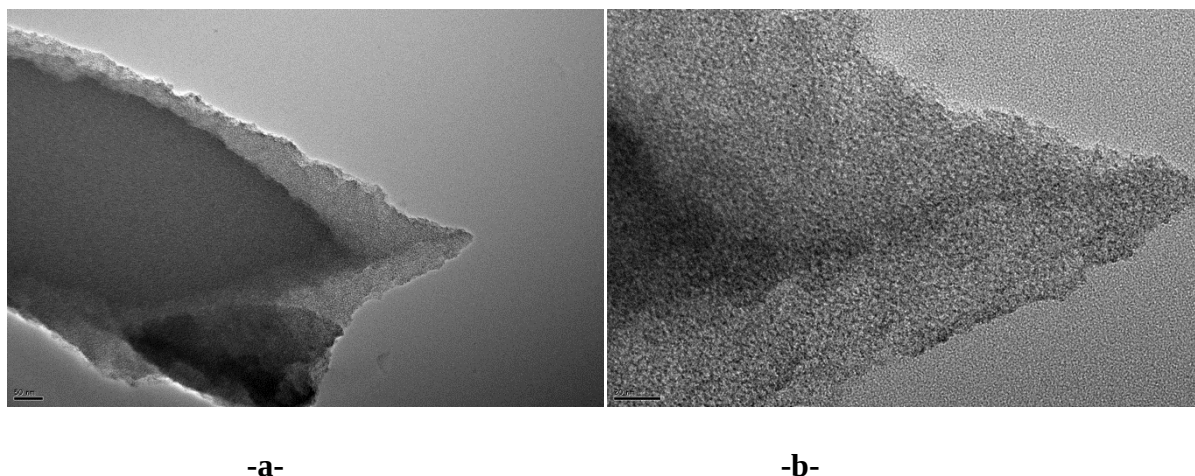


Figure 3.48 TEM images of mesoporous CoTiO_3 monolith (the scale bar is **a**) 50 and **b**) 20 nm).

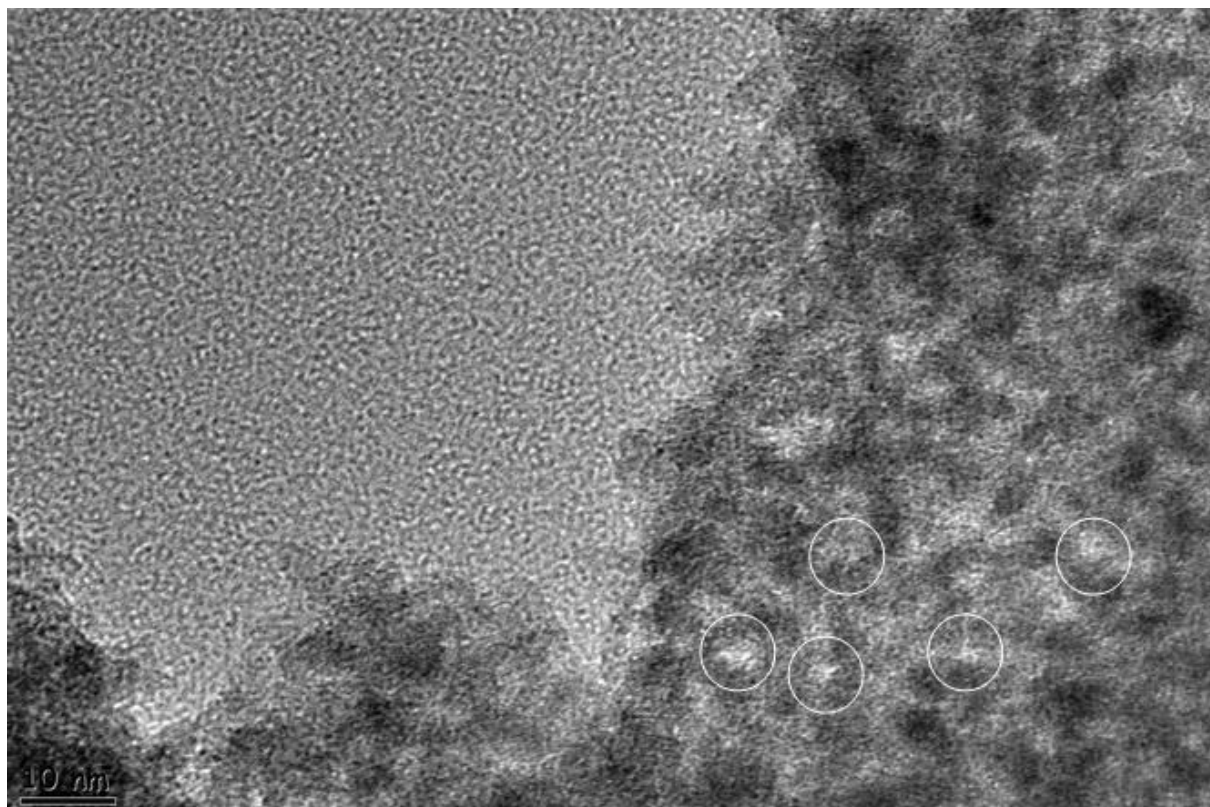


Figure 3.49 TEM image of mesoporous CoTiO₃ monolith (white circles show some the mesopores).

It is seen from **Figure 3.48** that the CoTiO₃ thin is homogeneously mesoporous throughout the whole structure and no bulk crystalline phase exists in the matrix. **Figure 3.49** is a closer look to the materials and it displays sponge-like feature with barely visible mesopores. Because the mesopores are disoriented throughout the film, it is difficult to determine the size of the pores. However, the minor contrasts, indicated with white circles, are attributed to the mesopores having diameters of no larger than 3-5 nm, a result which is in a good agreement with the N₂ sorption analysis.

Figure 3.50 shows the largely scaled TEM images of MnTiO₃ monolithic thin film piece calcined at 350 °C and scraped from a glass substrate. **Figure 3.51** is a closer view of the same sample.

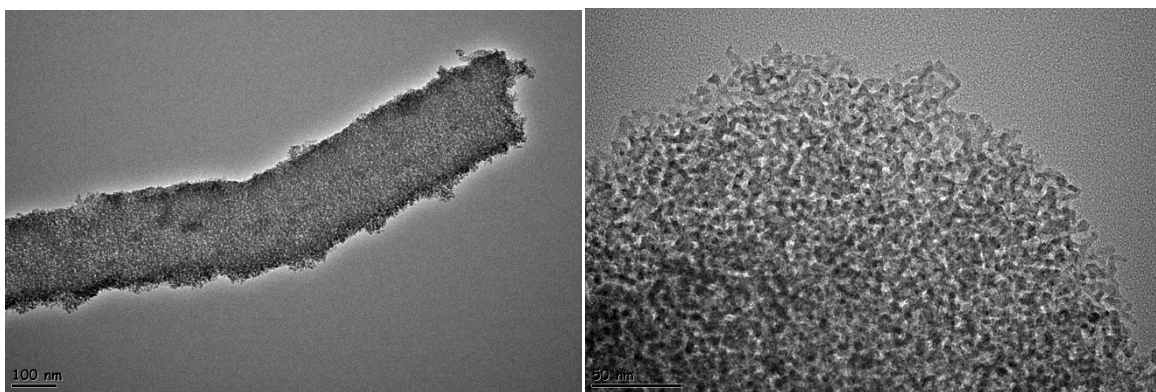


Figure 3.50 TEM images of mesoporous MnTiO_3 monolith

Similar to CoTiO_3 , MnTiO_3 displays a homogeneous sponge-like mesoporous structure without any secondary bulky phase throughout the thin film.

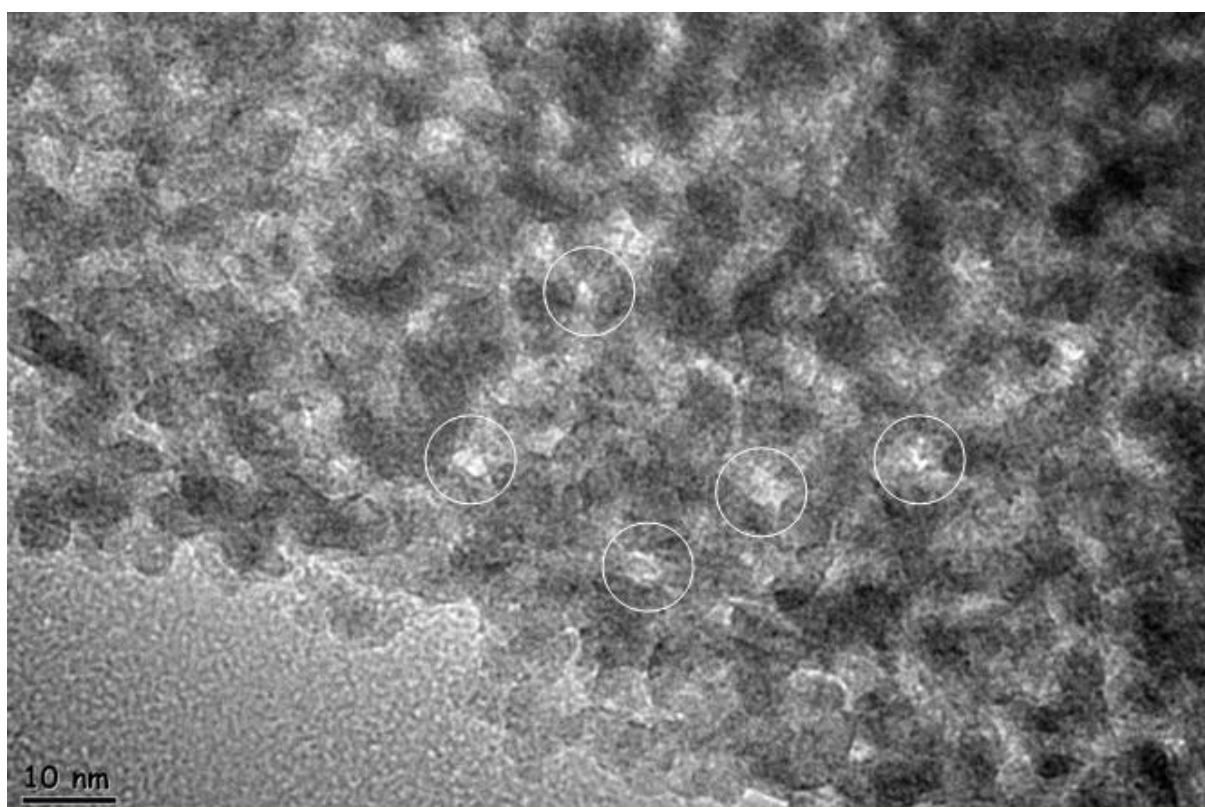


Figure 3.51 TEM image of mesoporous MnTiO_3 monolith (white circles show some of the mesopores).

The encircled areas in **Figure 3.51** are attributed to the homogeneously distributed mesopores with sizes ranging between 3-5 nm, also in a good agreement with the N_2 sorption measurements.

Figure 3.52 shows the largely scaled TEM images of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ monolithic thin film pieces calcined at 350 °C and scraped from a glass substrate. **Figure 3.53** is a closer view of the same sample.

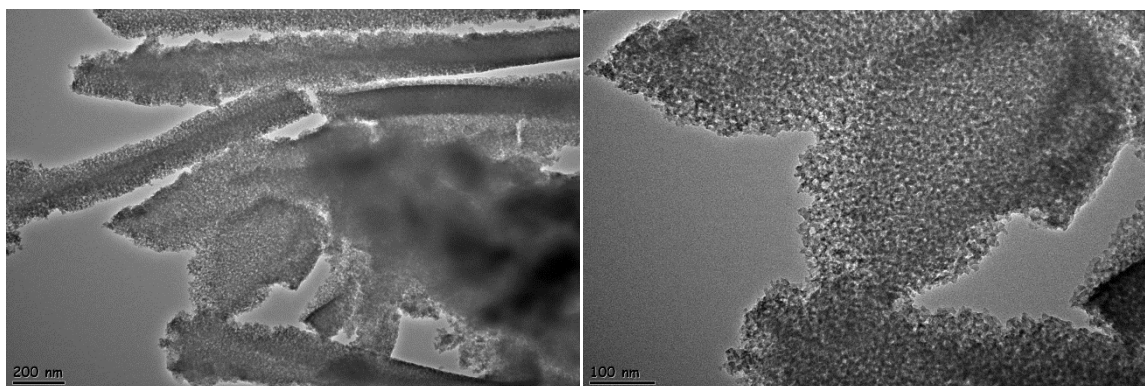


Figure 3.52 TEM images of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ monoliths

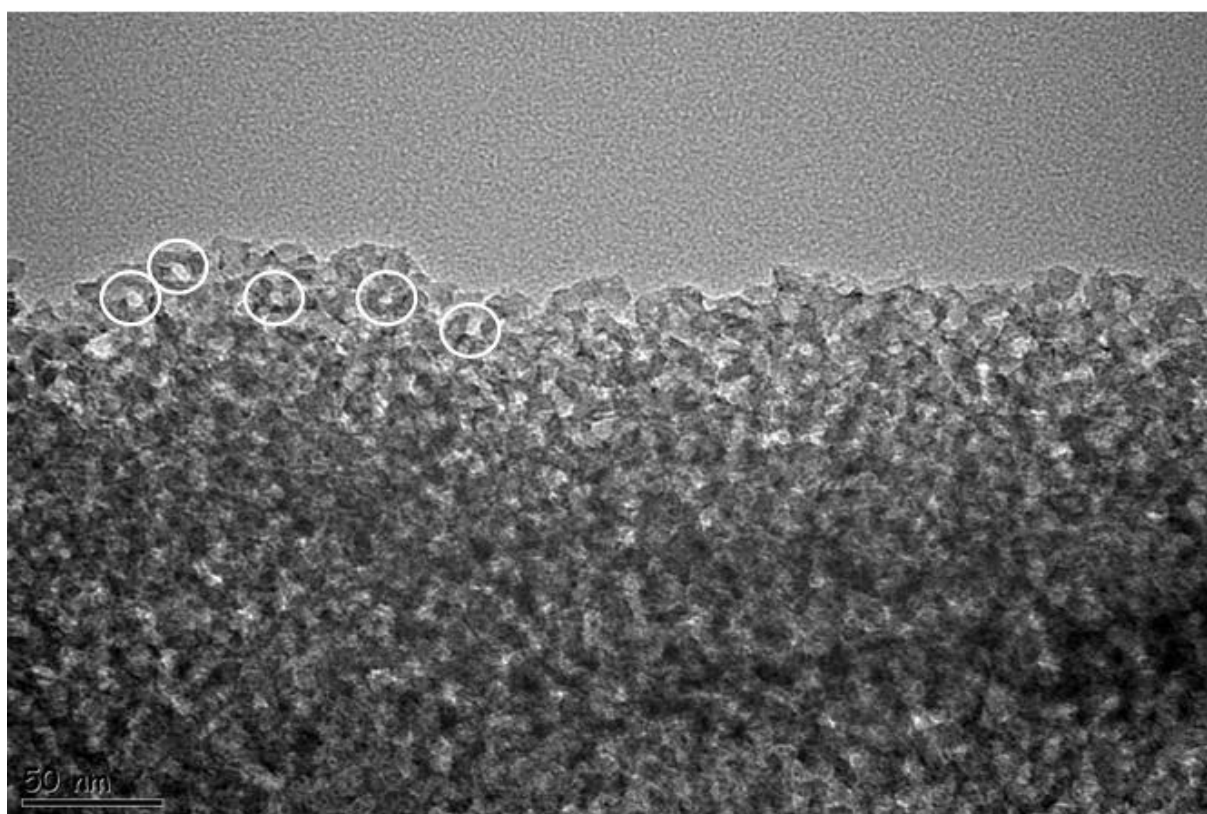


Figure 3.53 TEM image of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ monolith (white circles show the mesopores)

Mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ also displays good structural homogeneity throughout the thin film and disordered mesopores have sizes between 4-6 nm. The pores are slightly larger than the ones in CoTiO_3 and MnTiO_3 , a result which in a good agreement with N_2 sorption measurements.

As a result, all three materials displayed sponge-like mesoporous features with uniform pore size at their calcination temperature of 350 °C. However, notice that also all three materials went through a phase separation and structural collapse at 550 °C which led to a drastic decrease in the BET surface areas. **Figure 3.54** and **Figure 3.55** are TEM images of CoTiO₃ annealed step by step up to 550 °C.

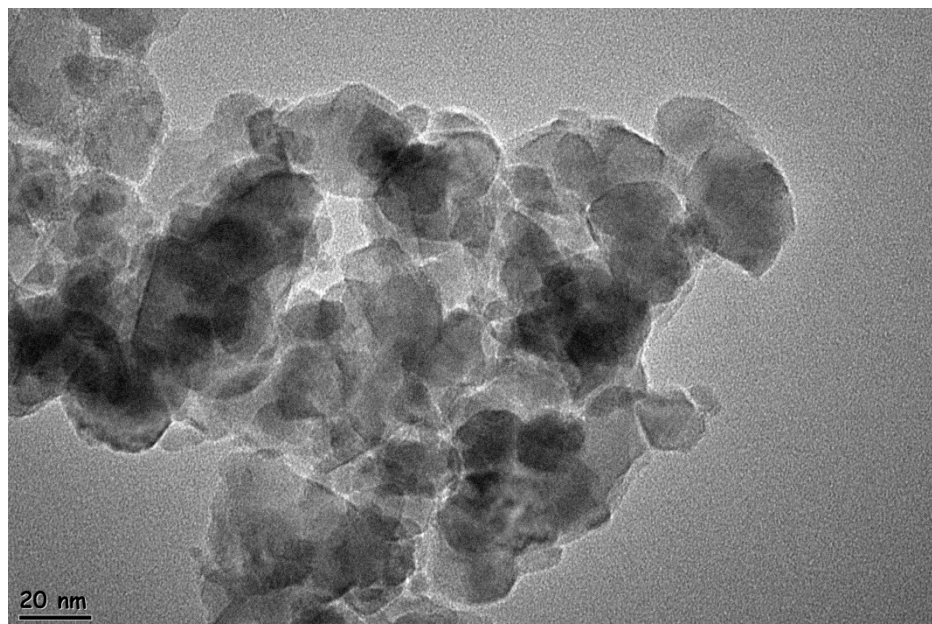


Figure 3.54 TEM image of CoTiO₃ annealed step by step up to 550 °C.

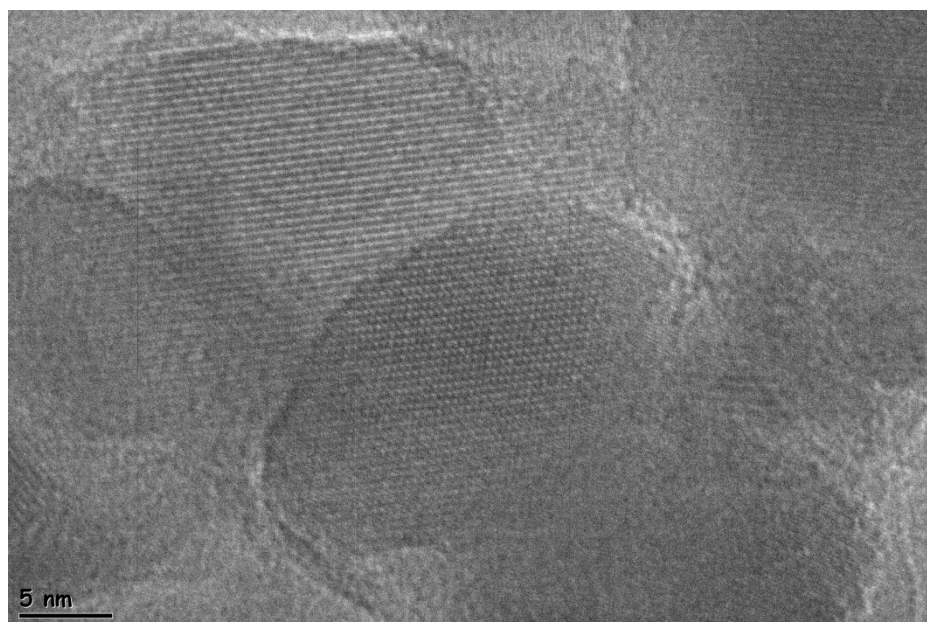


Figure 3.55 TEM image of CoTiO₃ annealed step by step up to 550 °C (closer view).

Notice that the structure observed in **Figure 3.54** is quite different from the structure observed in **Figure 3.48**. It is obvious that the sponge-like mesoporous feature has changed to a

nanocrystalline structure with crystal size of 20-40 nm. The lattice fringes are observable in **Figure 3.55**.

From the contribution of all characterization data combined together, it is seen that the pore size of mesoporous CoTiO_3 , MnTiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be tuned via easy post-calcination annealing steps. Materials with larger pore size and enhanced crystallinity can be achieved by sacrificing some of the surface area.

3.5. Effect of Direct Calcination vs. Step by Step Annealing on the Mesostructure

In the previous section, the response of the three mesoporous metal titanates to the post-calcination and annealing steps has been extensively discussed. In this part, another way of tuning the pore size of the mesoporous metal titanate thin films with enhanced pore wall crystallinity will be introduced.

It has already been mentioned in **section 3.3** that the change in the calcination route had no significant effect on the phase formation of mesoporous CoTiO_3 . Almost identical Raman spectra shown in **Figure 3.18** and **Figure 3.19** proved that at 350 °C, the time spent in calcination does not have any effect on the chemical structure. Therefore the calcination time had been decreased from 7 hrs to 15 min, an aspect which made MASA synthesis much more interesting. On the other hand, the calcination/post-calcination annealing route becomes much more relevant and decisive on the chemical and mesoporous structure of the final product when it comes to higher temperatures such as 550 °C. Notice that due to the fast calcination, MASA synthesis of mesoporous metal titanates happens in a very short time and depends on the removal of the template and formation of solid metal titanate network. At higher temperature, the chemical and physical structure is affected by the major change of the diffusion dynamics of species. By that means, one should expect to come up with different products by calcining as-prepared samples at different temperature.

Figure 3.56 shows the isotherms of 2 samples of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ monolithic powders prepared in the same conditions and calcined at 350 and 550 °C. It is observed from the isotherms in

Figure 3.56 that there is a change in the mesoporous structure upon the change in the calcination temperature. It is also observed from isotherms in **Figure 3.57** that all three samples which are; directly calcined at 550 °C (denoted as 550 °C(I)) , directly calcined at 550 °C then annealed at that temperature for another 2 hrs (550 °C(II)) and calcined at 350 °C then annealed step by step with 50 °C increment up to 550 °C (550 °C(III)), display different mesoporous structures.

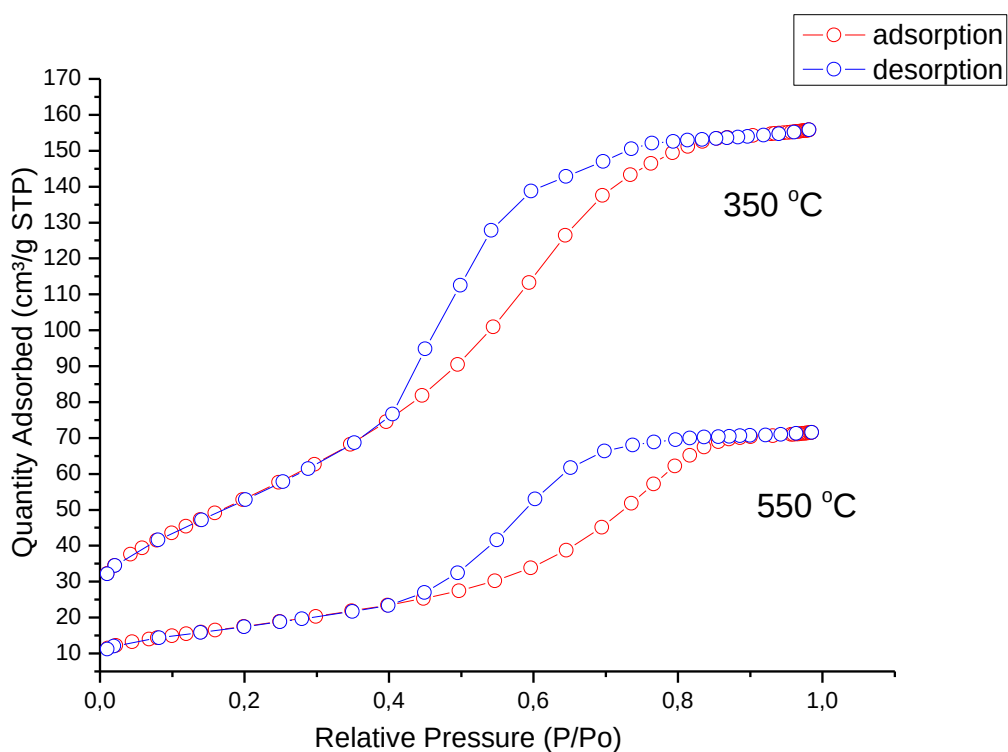


Figure 3.56 N_2 sorption isotherms of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ calcined at 350 and 550 °C.

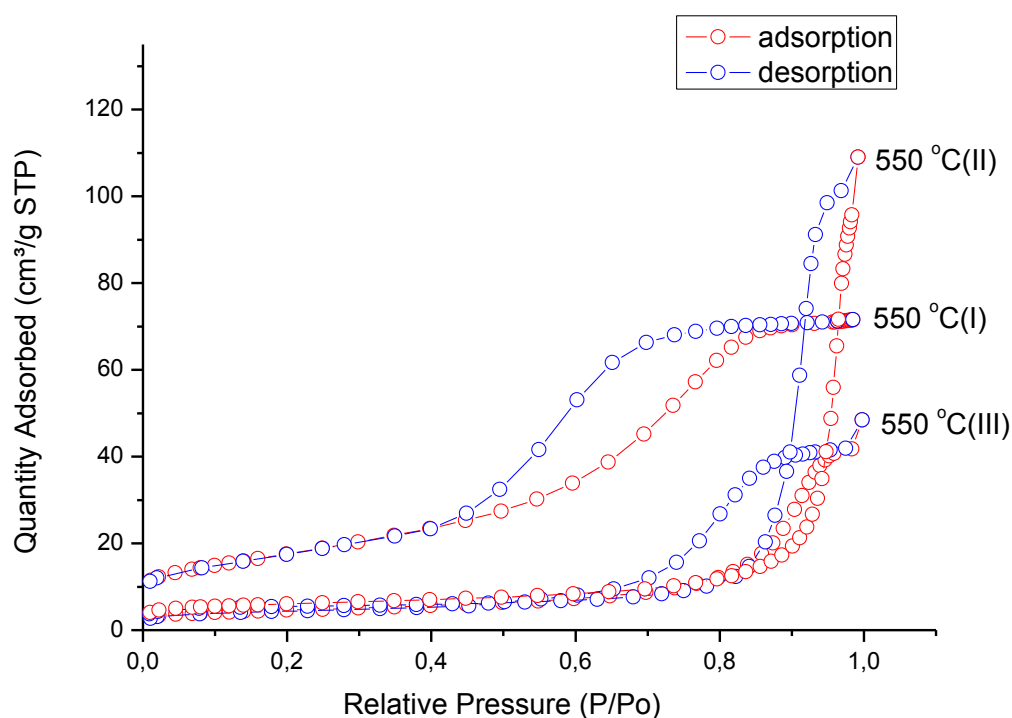


Figure 3.57 N₂ sorption isotherms of mesoporous Li₄Ti₅O₁₂ prepared with different calcination/annealing routes.

Table 3.5 summarizes all the N₂ sorption data calculated from the isotherms in **Figure 3.56** and **Figure 3.57**.

Table 3.5: N₂ sorption data of mesoporous Li₄Ti₅O₁₂ prepared with different calcination/annealing routes.

	BET Surface Area (m ² /g)	Mean Pore Size (nm)	Specific Pore Volume (cm ³ /g)
350 °C	193	4.3	0.25
550 °C(I)	63	4.7	0.11
550 °C(II)	16	9.4	0.07
550 °C(III)	21	22	0.17

As expected from previous explanations; 550(I), 550(II) and 550(III) display different properties especially in terms of pore size. On the other hand, the pore size of the sample calcined at 350 °C is surprisingly similar to the one calcined at 550 °C (350 °C: 4.3 nm and 550 °C(I): 4.7 nm). This result reveals the very important information about how the

calcination temperature governs the mesoporous structure. It seems like in MASA synthesis of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (and most probably of other titanates too), the calcination temperature does not have too much effect on the pore size, in other words, regardless to the calcination temperature (of course between 350 and 550 °C), the material starts with an almost unique pore size, which is guided by the surfactant micelles in the initial LLC phase. The change in the BET surface area and the pore volume between these two samples can be explained by the sintering and crystallization (closing of some of the pores) due to the faster diffusion of species on the near surface of the material.

It is also understandable from the pore size comparison of the samples 550(I), 550(II) and 550(III) that the annealing time plays a decisive role on the pore enlargement. Remark that the largest pore size achieved belongs to the sample 550 °C (III) which spent the longest time in the annealing oven (2 hrs at each annealing temperature from 400 to 550 °C, which makes a total 8 hrs). The sample 550 °C (II), which spent only 2 hrs at 550 °C, has a BET surface area similar to 550 °C (III). However, its pore size is less than half (9.4 nm) than that of 550 °C (III) (22 nm). This clearly shows that, materials with similar BET surface areas and different pore sizes can be obtained by simply playing with the calcination/annealing routes.

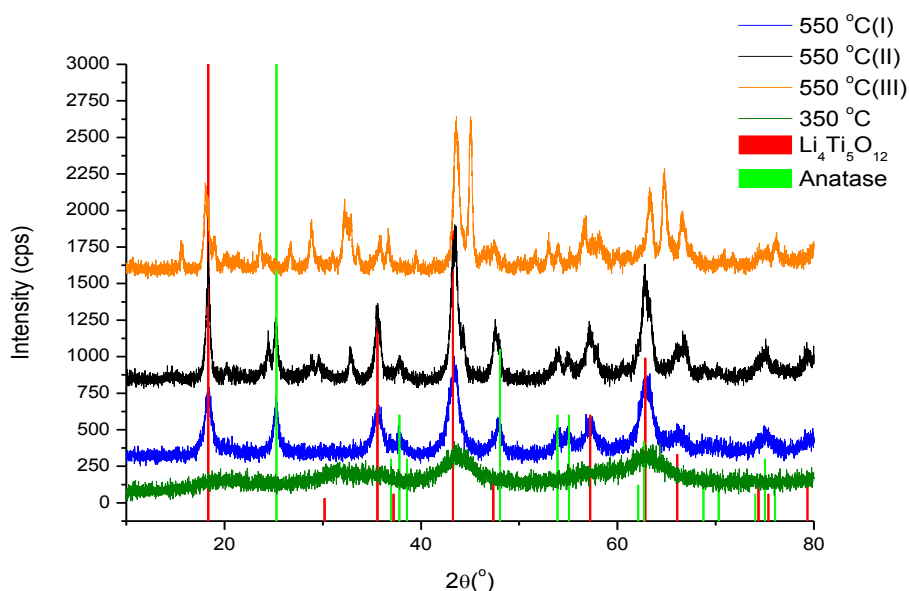


Figure 3.58 XRD patterns of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared with different calcination/annealing routes.

Figure 3.58 shows that these samples (shown in **Table 3.5**) are also different in terms of crystallinity. Remember that the XRD lines of the sample 550 °C (III) had not been assigned to any known phase of lithium titanate or titania. On the other hand, the samples 550 °C (I) and 550 °C (II) contains the well-defined phases of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and anatase TiO_2 (ICDD PDF #00-022-1272). It seems like the calcination route itself has an effect on the chemical structure as well as the pore size of the material. Another comparison should be made among the samples calcined at 350 and 550 °C (labeled as 350 °C and 550 °C (I), respectively, in **Figure 3.58**). At 350 °C, the sample exhibits broad XRD lines however; they get much sharper in 550 °C (I). This means that the sample which is directly calcined at 550 °C is much more crystalline than the one which is calcined at 350 °C and also, remember that their pore size were quite similar. From this point of view, it has been possible to synthesize two mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with almost identical phase and pore size but, with different pore wall crystallinities. Therefore one can conclude that while the crystallinity is a thermodynamic process, the pore-size expansion is a kinetic process and can be controlled by controlling the process time. Within this technique, one should only sacrifice from the surface area in order to obtain the same material with the same pore size but with enhanced crystallinity.

In this section it has been shown that, MASA synthesis does not only enable the production of mesoporous metal titanate thin films with record high BET surface areas, but also offers many simple ways to control the two important parameters of those materials such as pore size and pore wall crystallinity, almost independently from each other. Because, usually, the crystallization in the pore walls, leads to a growth of mesopores as well (see **section 3.4.3**). However, in this section, it has been demonstrated that it is possible to enhance the pore wall crystallinity by keeping the pore size constant.

3.6. Production and characterization of mesoporous metal titanate/graphite nanocomposite thin film

The work presented in this section is slightly different from the scope of the study reported so far. Remember from previous sections about optimizations on the synthesis condition, an unavoidable trace amount of Co_3O_4 was forming in the mesoporous CoTiO_3 matrix. To overcome this situation, the Co(II) source used in the initial solution is switched from the hydrous nitrate salt to anhydrous bromide salt of cobalt. The reaction temperature of bulk $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ with oxygen to form $\text{Co}_3\text{O}_4 + \text{NO}_x$ species is around 458 °C under N_2 atmosphere. [86] However, this temperature is surprisingly depressed under aerobic

atmosphere, and most importantly, due to the size confinement effect happening in MASA synthesis. This is the reason why Co_3O_4 is formed in the as-prepared samples even at low temperatures such as 240°C (**Figure 3.14**). On the other hand, CoBr_2 is known to be stable to O_2 reaction even at 678°C , which is the melting point of bulk anhydrous CoBr_2 . [87] In order to see the reaction behaviour of CoBr_2 with oxygen, a series of Raman spectra of both bulk $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ and CoBr_2 have been collected. **Figure 3.59** shows the Raman spectra of bulk forms of: CoBr_2 without any treatment, CoBr_2 calcined at 350°C , $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ calcined at 350°C and CoBr_2 calcined at 700°C . The peaks observed at 941 , 463 , 242 , 154 and 87 cm^{-1} in the Raman spectrum of room temperature bulk CoBr_2 are phonon and due to Raman active modes of CoBr_2 . [88] It is seen from the second spectrum which belongs to CoBr_2 calcined at 350°C that CoBr_2 does not react with oxygen at 350°C either. At the same spectrum, some small peaks around 680 , 512 and 468 cm^{-1} are attributed to Co_3O_4 , possibly formed in a small quantity on the surface of the CoBr_2 powder. On the other hand, seen from the peaks around 675 , 610 , 510 , 463 and 190 cm^{-1} which are attributed to the Raman modes of Co_3O_4 [73], $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ got already transformed to Co_3O_4 at 350°C . It is also seen that CoBr_2 reacted with oxygen to form Co_3O_4 at 700°C .

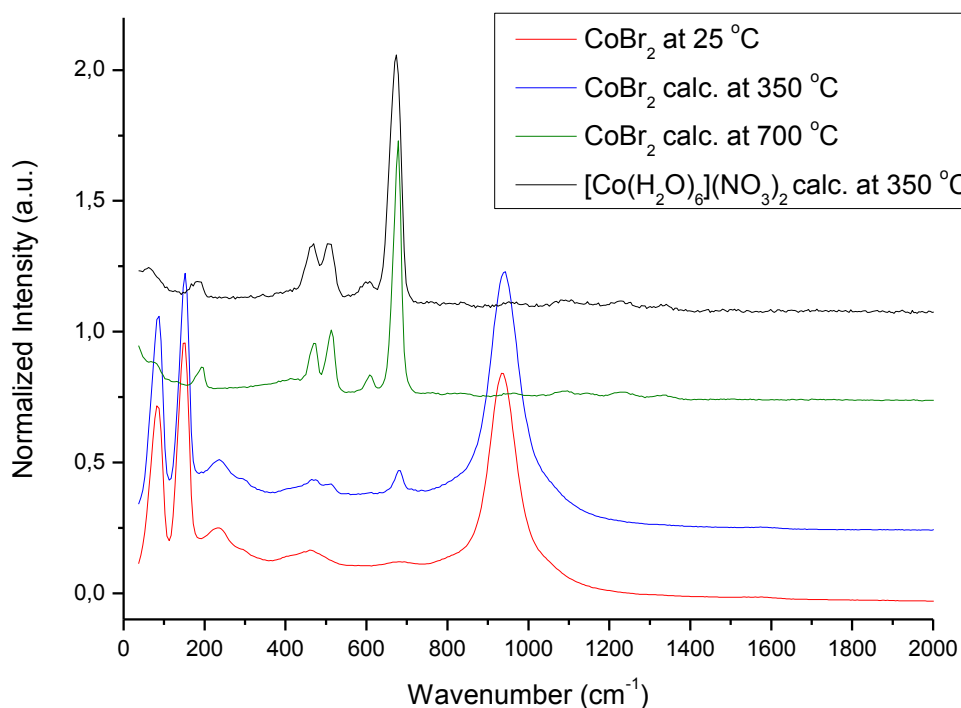


Figure 3.59 Raman spectra of bulk CoBr_2 without any treatment, CoBr_2 calcined at 350°C , $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ calcined at 350°C and CoBr_2 calcined at 700°C .

Due to the fact that CoBr_2 is less reactive under oxygen atmosphere than $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ at lower temperatures, the formation of Co_3O_4 might be hindered at low calcination temperatures such 220, 300 and 350 °C. **Figure 3.60** shows the Raman spectra recorded from the surface of the films of CoTiO_3 prepared using CoBr_2 , as Co(II) source.

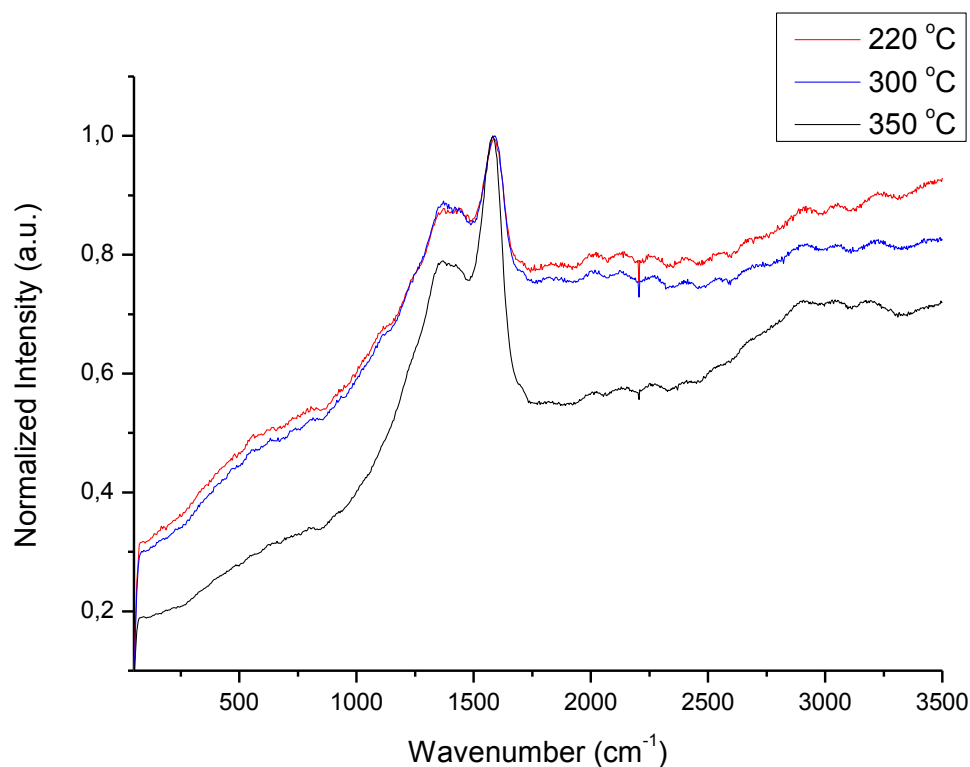


Figure 3.60. Raman spectra recorded from the surface of the CoTiO_3 films calcined at different temperatures and prepared using CoBr_2 as Co(II) source.

All three Raman spectra are quite similar to each other and no sign of Co_3O_4 formation is observed. However, the two broad peaks positioned around 1380 and 1580 cm^{-1} are surprisingly attributed to the well-known D and G bands of graphite. [89] Moreover, the conventional graphitization of carbon for producing mesoporous graphite using precursors made of hydrocarbons requires autoclaving at very high temperatures and inert atmospheres. [90] [91] [92] [93] [94] Many efforts have been put so far, to develop a low temperature path to obtain mesoporous graphitized carbon. [95] [96] [97]

In the mesoporous CoTiO_3 thin film, it seems like there is a metal oxide catalysed graphitization occurring in the material at the nano- or even sub-nanoscale. On the other hand, because the phenomenon has not been observed in the previously synthesized CoTiO_3 materials prepared using nitrate salt, the effect of Br^- to the catalysis of graphite formation

should not be ignored. A possible explanation can be made by putting forward the idea of the possible oxidation of Br^- leading to the reduction of hydrocarbon species to form a carbonized structure. Besides, it should be noticed that the carbonized structure is not totally graphitized. The Raman peak rising around 1380 cm^{-1} is an indication to the existence of a structure named glassy carbon. [98] The D band, also referred as the “defect mode”, corresponds to sp^3 diamond-like carbon structures and, the G band corresponds to sp^2 graphitic structures. [99] It is observed from the Raman spectra of CoTiO_3 that the intensity ratio of the D peak over G peak (I_D/I_G) is higher in the samples calcined at 220 and 300 °C compared to one calcined at 350 °C. The decreasing of the I_D/I_G ratio is a clear sign for graphitization in carbon structures. [97] It is also well-known that graphitization of glass-like carbon is a hard procedure which requires a lot of energy and time. Therefore, the effect of the confinement in a very small area coupled with the effect of the close contact of the catalyst in the atomic level is probably the answer of this unexpected fast formation of graphite at low temperatures. The broader peak around 3000 cm^{-1} in the spectrum of the sample calcined at 350 °C, is the overtone (G_2 band) of the first G band. This is another indication for graphitization of the glassy carbon structure at higher calcination temperatures. **Figure 3.61** shows the Raman spectra recorded from the scraped powder of the same mesoporous CoTiO_3 thin films shown in **Figure 3.60**.

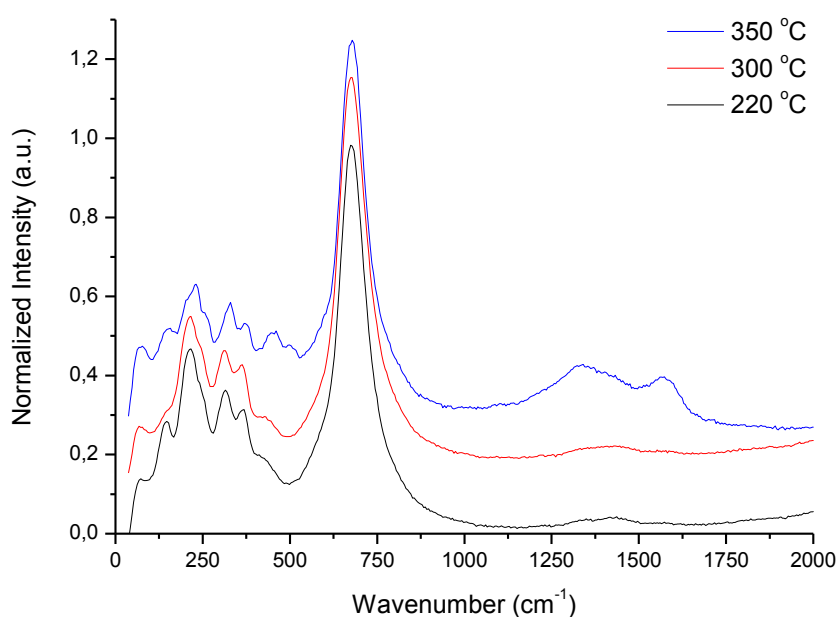


Figure 3.61 Raman spectra recorded from the scraped powder of the CoTiO_3 films calcined at different temperatures and prepared using CoBr_2 as Co(II) source.

Collecting Raman signals from the scraped powder of the thin films means that, average information is collected from the whole material of the film. This is why the Raman signals of carbon which are clearly observed in **Figure 3.60**, are not that much visible in the spectra in **Figure 3.61**. However, in the spectrum of the sample calcined at 350 °C, both D and G peaks are visible. Also notice that, in this sample, the I_D/I_G ratio (which is more than 1) is quite different from the one in the spectrum taken from the surface of the film. This probably shows that, because the Br^- anions leave the structure as Br_2 from the very surface, the catalysed graphitization is favoured over glassy carbon formation on the near surface of the film. This also explains why the G band is much more intense compared to the D band on the surface than in the depth of the mesoporous thin film.

The two spectra belonging to the samples calcined at 220 and 300 °C exhibit typical Raman spectra of mesoporous CoTiO_3 (as reported in the previous sections). At 220 °C, in addition to the CoTiO_3 related peaks; there is a small peak around 150 cm^{-1} attributed to the anatase phase of TiO_2 , probably left in a trace amount, unreacted with CoBr_2 due to the low calcination temperature. Another evidence of Br^- being responsible for this graphitization can be seen from the spectrum of the sample calcined at 350 °C. Two new peaks rising around 508 and 465 cm^{-1} are characteristic for Co_3O_4 and it seems like the population of graphite increases as well as the Co_3O_4 is formed. It has been already mentioned that the oxidation of Br^- triggers the carbonization. This oxidation of Br^- occurs in oxygen atmosphere and, CoBr_2 reacts with oxygen to form Co_3O_4 and Br_2 . The process of Co_3O_4 formation is simultaneous with the Br^- oxidation and by extension, the carbonization of hydrocarbon species. Therefore, the formation of Co_3O_4 can be considered as a good probe to trace the carbonization.

The carbonization in the mesoporous CoTiO_3 thin films occurs in two ways; graphitization on the near-surface and formation of glassy carbon throughout the bulk of the film. In this regard, the majority of the carbon material in the film exists as glassy carbon. An indirect way of characterizing this glassy carbon in the almost amorphous mesoporous network is to observe its effect on the mesoporous feature of the material. It is known that glassy carbon is a nonporous material which is impermeable to any gas adsorption. Therefore, if the carbonization is driven by the oxidation of Br^- , the increase in the Br^- content in the material should increase the amount of glassy carbon in the structure and as a result, the specific surface area of the mesoporous CoTiO_3 thin film should decrease gradually. In order to observe this, an experiment is designed and 5 samples with increased proportion of CoBr_2 are prepared (see **Table 2.1**) for the sample names and contents) by keeping the Co(II):Ti(IV)

ratio constant at all samples. It means that CoBr_2 is mixed with $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ in different percentages but the amount of the $\text{Co}(\text{II})$ in the initial solution is kept constant. **Table 3.6** shows the N_2 sorption data collected from the samples prepared using different $\text{CoBr}_2:[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ mole ratios.

Table 3.6: N_2 sorption data of mesoporous CoTiO_3 monolithic powders prepared using different $\text{CoBr}_2:[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ mole ratios.

	BET Surface Area (m^2/g)	Mean Pore Size (nm)	Specific Pore Volume (cm^3/g)
CT4A	318	3.1	0.26
CT4AB1	302	2.5	0.18
CT4AB2	264	3.0	0.24
CT4AB3	238	2.6	0.17
CT4B	110	2.8	0.07

There is a clear decrease in the BET surface area in the samples prepared using more CoBr_2 over $\text{CoBr}_2:[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$. One may argue that this decrease is due to the glassy carbon existing in the mesoporous CoTiO_3 . However, this speculation might not be valid and the reason to this decrease in the surface area might be a result of bulky CoBr_2 recrystallization. Normally, CoTiO_3 is a wide band gap semiconductor with low electrical conductivity. [100] Some preliminary studies showed the electrical conductivity of CoTiO_3 is increased by a factor of 1000 when CoBr_2 is used as the $\text{Co}(\text{II})$ source. Apart from the drastic increase in the conductivity, another clue supporting the idea of the glassy carbon being nano-incorporated in the mesoporous CoTiO_3 matrix is that the thin films produced in this way have the same colour and are just as transparent as the regular mesoporous CoTiO_3 thin films. However, no matter how strong the evidences are, this is for now nothing more than a speculation based on some insufficient characterization. On the other hand, what is certain that, the presence of carbonized structures is evident by the Raman spectra and the decrease of the surface area is observed upon the increase in CoBr_2 used in the initial solution.

As a result, despite some lacking characterizations, it would not be wrong to say that a mesoporous graphite/glassy carbon/ CoTiO_3 nanocomposite is formed via MASA synthesis and Br^- driven catalysed carbonization of the surfactants.

4. CONCLUSION

It has been shown that MASA synthesis is a facile and yet, powerful method to produce mesoporous CoTiO_3 , MnTiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin films with a high optical transparency. The materials calcined at 350 °C displayed a BET surface area as high as 193, 318 and 445 m^2/g , respectively and the pore size distributions were quite narrow. In their respective category, these results are by so far, the highest achieved among the mesoporous metal titanate thin film materials.

Several optimizations such as; setting the salt:surfactant ratio and the amount acid in the initial solution, and the determination of calcination/annealing route have been done in the flow of the synthesis path. It has been observed that the amount of acid and the salt:surfactant ratio in the initial solution is crucially important for the stabilization of the initially formed mesophase (i.e. as-prepared LLC films). The orientation and the meso-order of the LLC phase of the as-prepared films affect directly the mesoporosity and the pore size distribution of the final mesoporous metal titanate thin films. It has been found that the pore size can be controlled and the pore wall crystallinity can be enhanced by performing simple annealing procedures between 350 and 500 °C, without damaging the mesoporous network. At 550 °C, CoTiO_3 and MnTiO_3 went through a phase separation to their component metal oxides ($\text{Co}_3\text{O}_4/\text{TiO}_2$ and $\text{Mn}_2\text{O}_3/\text{TiO}_2$ respectively), accompanied with a structural collapse which led to a drastic decrease in the BET surface areas (318 to 52 m^2/g and 445 to 33 m^2/g , respectively). Again at 550 °C, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ undergoes a phase transition to an unknown $\text{Li}_x\text{Ti}_y\text{O}_z$ compound, with a similar structural collapse where the BET surface area decreases from 193 to 21 m^2/g . In the safe temperature range (350-500 °C), the pore size of the mesoporous CoTiO_3 , MnTiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ increase from 3.1, 3.2 and 4.2 nm to 5.6, 5.4 and 9.9 nm, respectively. The mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is more distinct and, it shows higher pore wall crystallinity than CoTiO_3 and MnTiO_3 at all temperatures.

It is also important to note that by simply switching the Co(II) salt from $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ to CoBr_2 in the MASA synthesis; carbonization of the surfactant species can be promoted in the mesoporous CoTiO_3 . Moreover, the carbonization occurs at extremely low temperatures, as low as 220 °C, under air atmosphere. The MASA synthesis route is not limited to metal titanates, other metal oxides can be prepared for various purposes.

5. FUTURE WORKS

In order to show that MASA synthesis is not limited to only metal oxide/silica or metal titanate thin films materials, the same route for sample preparation described in the experimental section has been applied for the production of LiMn_2O_4 and LiCoO_2 thin films. Generally, the same procedure for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is followed except that the titanium(IV)butoxide is switched to $[\text{Mn}(\text{H}_2\text{O})_4](\text{NO}_3)_2$ or $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ for the synthesis of LiMn_2O_4 and LiCoO_2 .

LiCoO_2 crystallizes in hexagonal and cubic structure. The cubic structure often referred as layered structure, is highly suitable for Li^+ ion intercalation. However, this phase is formed at high temperatures such as 900°C and it usually crystallizes in the bulk form. On the other hand, the hexagonal-spinel phase, which is less suitable for Li^+ ion intercalation, is formed at low temperatures such as 450°C and can be tailored into nanostructures. [101]

LiMn_2O_4 exists in a cubic-spinel structure at all temperatures. It has been also reported that tetrahedral and monoclinic-spinel phases also exist. [102] However, being highly unstable, the structure transforms into cubic-spinel phase immediately.

The XRD study for characterizing the LLC phase formation is done for Li(I):Mn(II) samples (**Figure 5.1**).

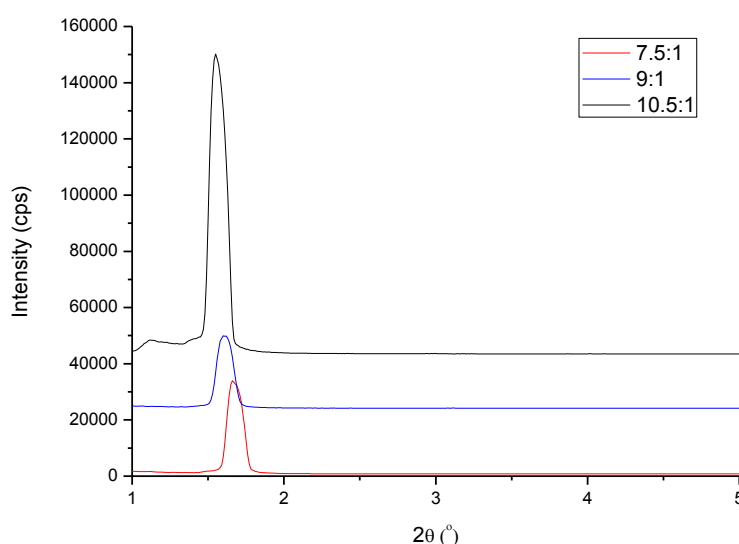


Figure 5.1 Small angle XRD patterns of as-prepared Li(I):Mn(II) samples with different salt:surfactant mole ratios

It is observed that $\text{Li(I):Mn(II):C}_{12}\text{EO}_{10}$ can form the LLC phase and the d-spacing is expectedly expanding upon the increase of the salt:surfactant mole ratio. This study showed that, a polymerizing agent such titanium(IV)butoxide is necessarily needed for LLC formation. It is also seen that the LLC phase can support as high as 10.5:1 of salt:surfactant ratio.

5.1. LiMn_2O_4

A sample with 1.5:3:1 of $\text{Li(I):Mn(II):C}_{12}\text{EO}_{10}$ (which makes a total of 4.5:1 salt:surfactant ratio) is prepared and calcined at 450 °C and shows the Raman spectra taken from the surface and the inner bulk of the film.

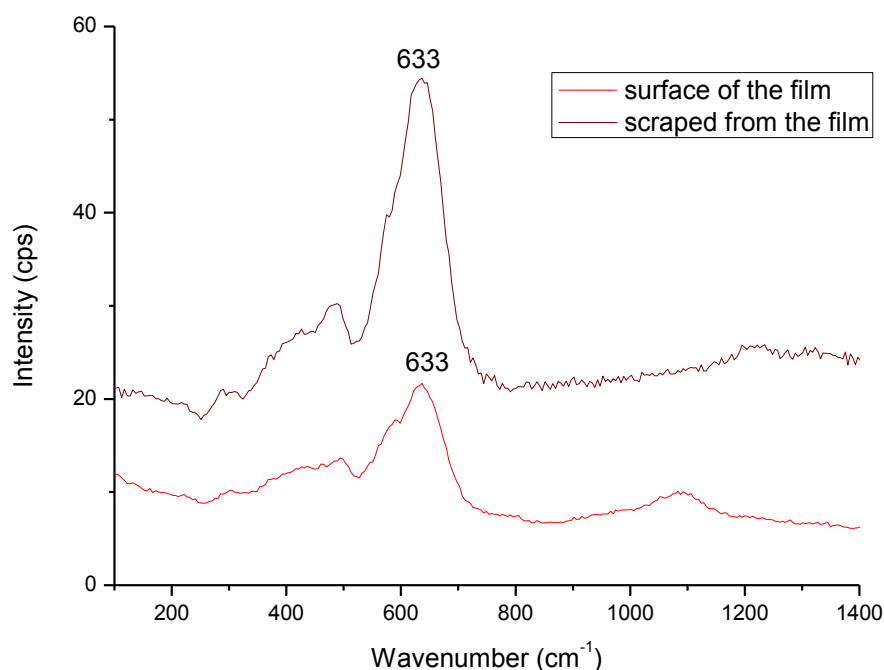


Figure 5.2 Raman spectra of LiMn_2O_4 samples.

Both spectra collected from the surface and inner bulk of the film display a very unique peak around 633 cm^{-1} , which is in accordance with the only Raman mode of spinel LiMn_2O_4 . [103] [104] [105]

Figure 5.3 and **Figure 5.4** show the TEM images of LiMn_2O_4 at different scales.

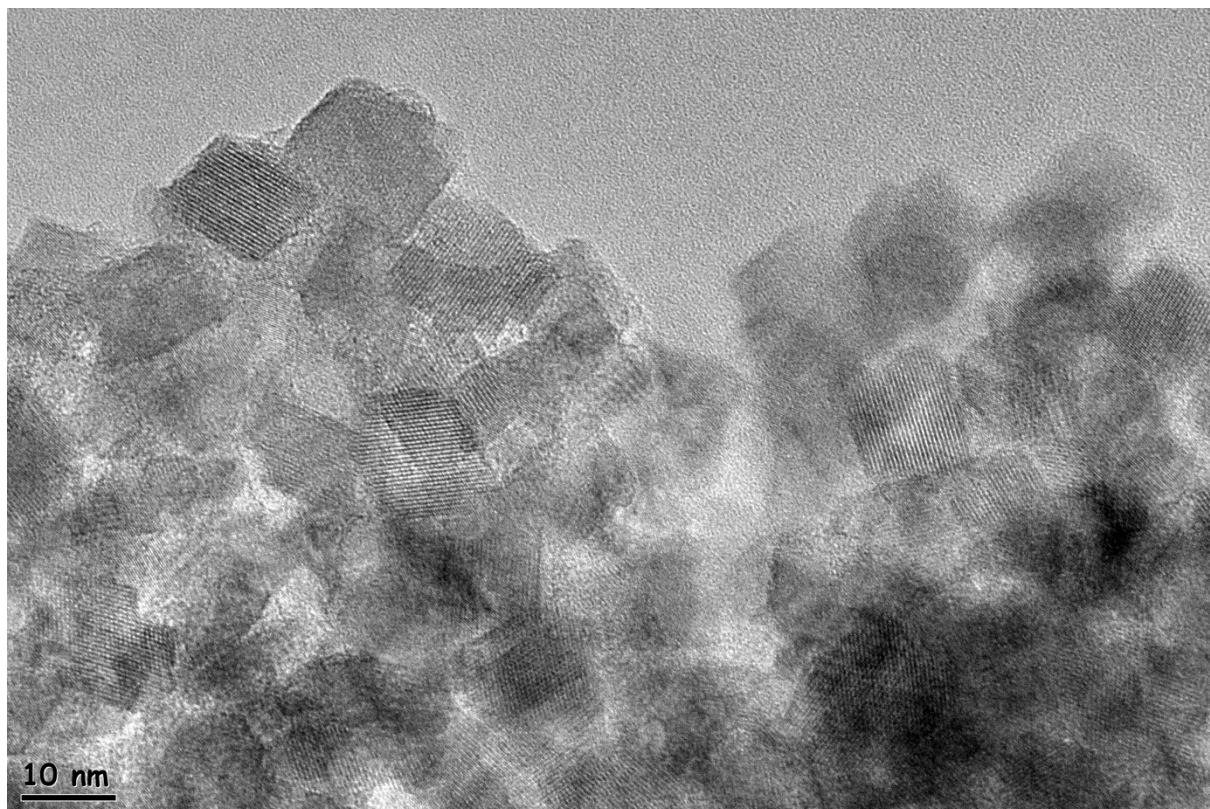


Figure 5.3 TEM image of a LiMn₂O₄ monolith.

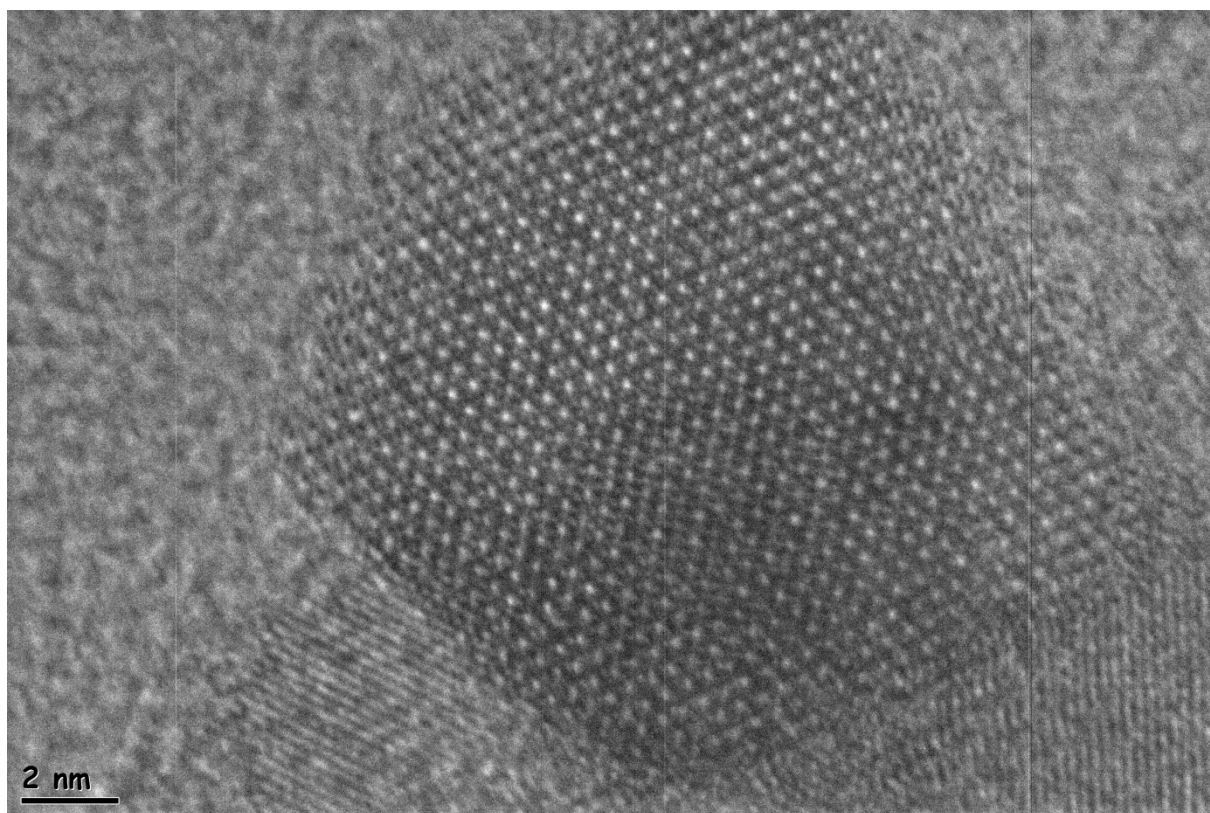


Figure 5.4 TEM image of a single LiMn₂O₄ crystal domain

Crystals with easily distinguishable lattice fringes having sizes around 10-20 nm refers to a nanocrystalline LiMn_2O_4 formation. Notice that the structure is not spongy-like mesostructure and the morphology is quite different from the previously shown mesoporous metal titanates. However, nanocrystals with such homogeneously distributed sizes, and of course in the form of thin film, are still interesting materials which can be further optimized.

5.2. LiCoO_2

One of the challenges in the production of LiCoO_2 is to manage to produce the layered structure (also referred as high temperature (HT) structure) at lower temperatures. **Figure 5.5** shows the Raman spectrum of the LiCoO_2 thin film coated on a stainless steel substrate and calcined at 450 °C.

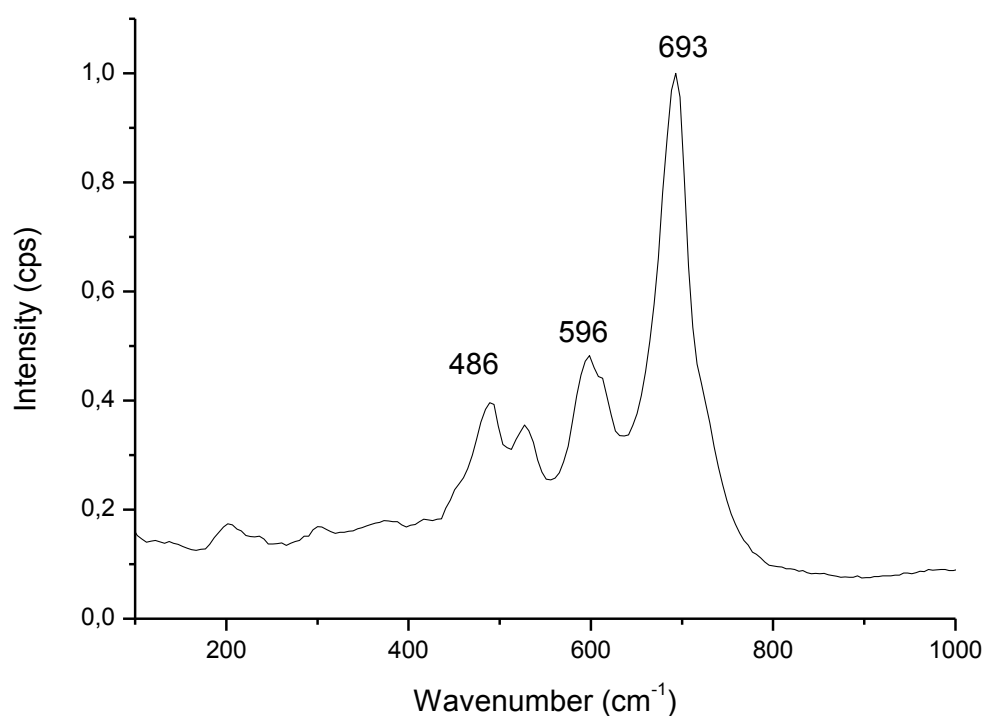


Figure 5.5 Raman spectrum of the LiCoO_2 thin film coated on a stainless steel substrate.

Layered LiCoO_2 has two Raman modes at around 597 and 487 cm^{-1} and spinel LiCoO_2 has four Raman modes at 449, 484, 590 and 605 cm^{-1} . [101] In the spectrum shown in **Figure 5.5**, four Raman modes are located around 693, 596, 530 and 486 cm^{-1} . Obviously, the synthesized LiCoO_2 is not in the spinel phase. On the other hand, the two of modes observed

are well matching with reference data. The two other modes observed around 693 and 530 cm^{-1} probably belongs to an unknown surface oxide from the stainless steel because the those two peaks does not match with the Raman modes of a possibly formed Co_3O_4 either. Therefore, with MASA synthesis, the layered phase of LiCoO_2 is formed at 450 $^{\circ}\text{C}$.

Figure 5.6 shows an SEM comparison of two LiCoO_2 materials, one synthesized using MASA and the other synthesized without using surfactants.

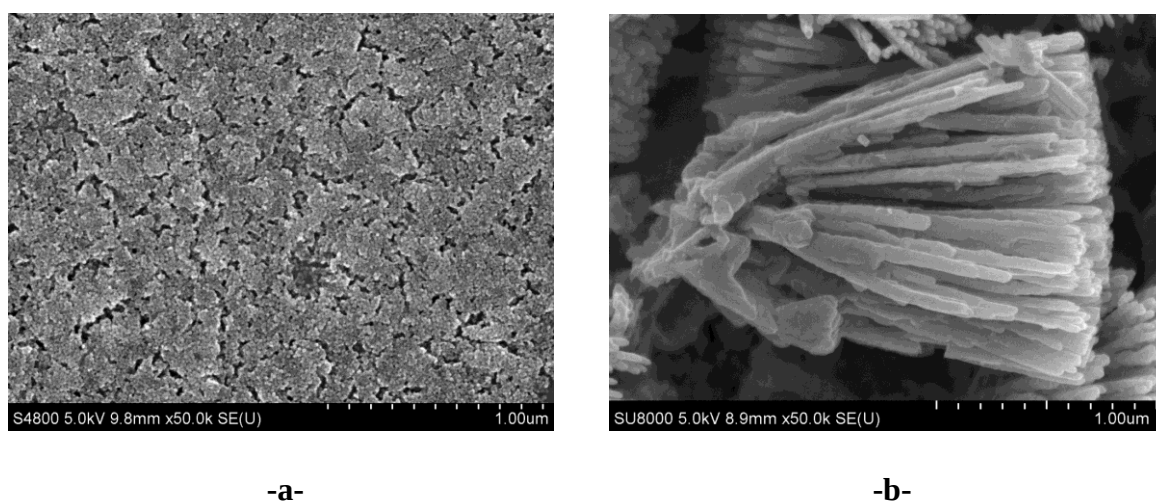


Figure 5.6. LiCoO_2 material synthesized **a)** using MASA and **b)** without using surfactants

Based on the SEM images, it is observed that there is a clear difference in LiCoO_2 materials synthesized using and not using MASA. The first material displays fine granular structure with small crystallites; the second material constitutes of micron sized bulk crystals. **Figure 5.7** shows an SEM image of LiCoO_2 at a higher magnification.

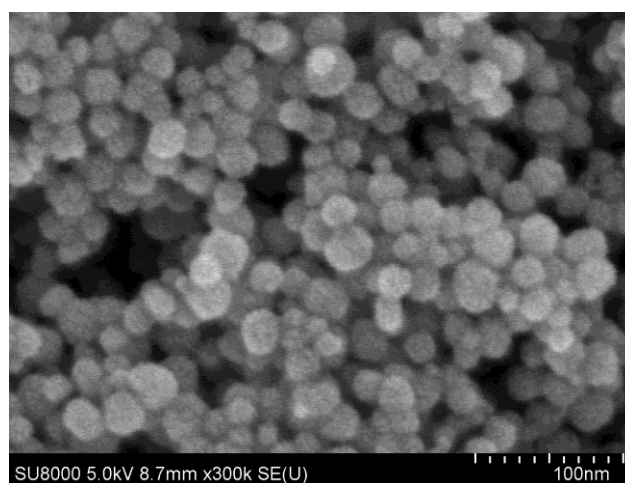


Figure 5.7 SEM image of LiCoO_2

LiCoO₂ synthesized via MASA approach exhibits nanocrystalline structure similar to LiMn₂O₄ with crystal size around 20 nm. The TEM image (**Figure 5.8**) also shows that the nanospherical feature observed in the SEM (**Figure 5.7**) display polycrystalline structure in itself.

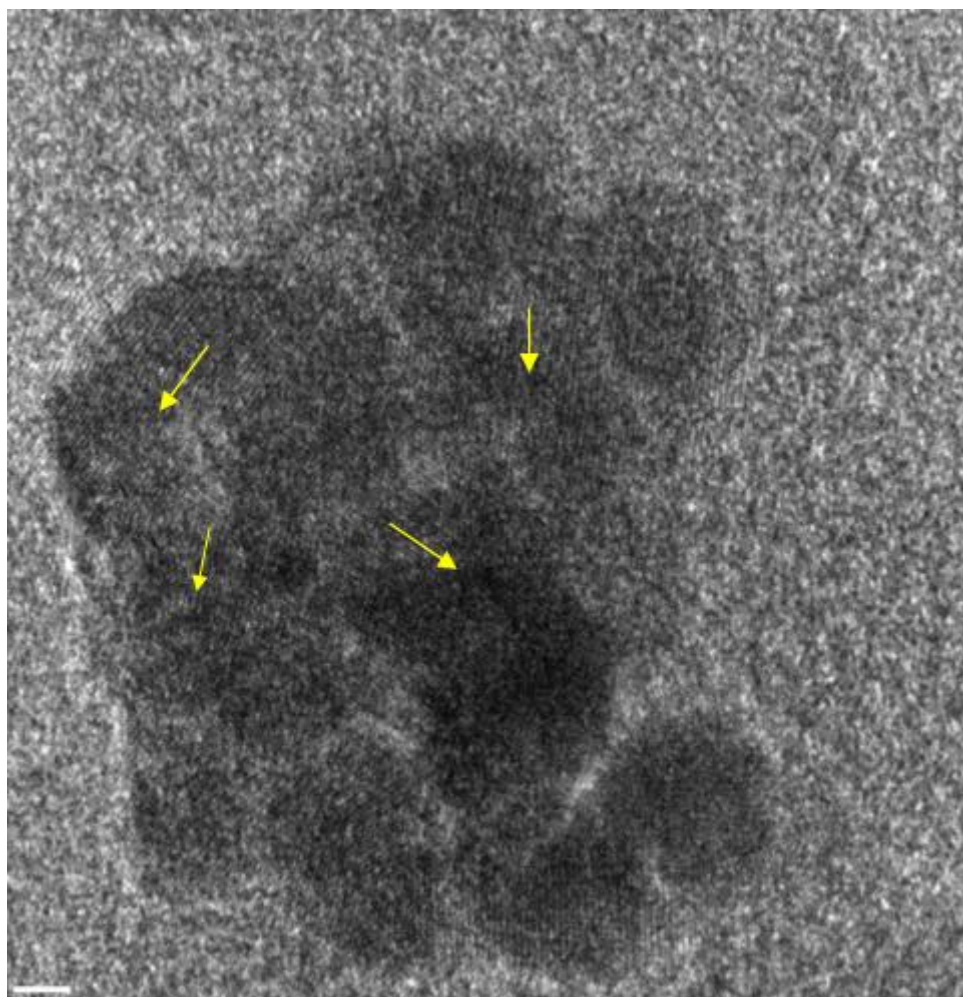


Figure 5.8 TEM image of a single LiCoO₂ nanospherical feature (Scale bar is 2 nm).

As a summary, based on the preliminary Raman Spectroscopy, SEM and TEM characterizations; highlighted materials such as nanostructured LiCoO₂ and LiMn₂O₄ thin films can be synthesized using MASA approach. Spinel LiMn₂O₄ and the interesting layered LiCoO₂ can be produced at low temperatures. Despite the fact that these synthesized materials do not exhibit spongy-like mesostructures, they are still promising due to their nano-sized features. However, further optimizations and characterizations are needed for a step forward.

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