

**SYNTHESIS AND CHARACTERIZATION OF
MESOPOROUS CADMIUM TITANATE THIN FILMS**

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SYNTHESIS AND CHARACTERIZATION OF MESOPOROUS CADMIUM TITANATE
THIN FILMS

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We certify that we have read this thesis and that in our opinion it is fully adequate,
in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF MESOPOROUS CADMIUM TITANATE THIN FILMS

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This thesis work focuses on the synthesis and characterization of mesoporous CdTiO_3 thin films by using a salt-surfactant assembly, which is defined as molten salt assisted self-assembly (MASA) method. The MASA method is a proper process to fabricate mesoporous transparent thin films. The characterization of the calcined powder and fresh gel samples was made by using XRD, SEM, TEM, ATR-IR, N_2 sorption and POM techniques.

The preparation of a clear solution containing ethanol as solvent, $[\text{Cd}(\text{H}_2\text{O})_4](\text{NO}_3)_2$, two different surfactants ($(\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3)\text{Br}$ and $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$), titanium(IV)butoxide ($\text{Ti}(\text{OC}_4\text{H}_9)_4$) as titania source and concentrated HNO_3 as acid to prevent quick polymerization of titanium alkoxide is the first step for the synthesis of the desired material.

The prepared clear solution is coated on the glass substrates to form a liquid crystalline mesophase by the hydrolyzed titania species and the molten salt by the guidance of surfactant domains. Upon the calcination of the fresh gel samples, mesoporous CdTiO₃ material is formed. In scope of this thesis work, several parameters were changed to determine the optimum the salt uptake, acid amount, surfactant ratio, coating method and calcination path for the synthesis.

Among dip coating, spin coating and drop casting methods, dip coating method gave better results to produce a material with less side products, which was mainly CdO. The amount of HNO₃ added to the solution affects the homogeneity and stability of the prepared fresh films. Although changing the amount of HNO₃ did not affect the surface area significantly, it was observed that addition of excess amount of acid resulted in an uneven surface on calcined films. CdTiO₃ is nanocrystalline at 350°C and stable up to 550°C. The initial calcination temperature is an important parameter to synthesize a material with less side product. Mesoporous CdTiO₃ displays 44 to 79 m²/g surface area and pore volume of 0.11 to 0.18 cm³/g depending on the synthesis conditions.

Keywords: Mesoporous thin films, CdTiO₃, Molten Salt Assisted Self-Assembly (MASA).

ÖZET

**MEZOGÖZENEKLİ CdTiO₃ İNCE FİLMLERİN SENTEZİ VE
KARAKTERİZASYONU**

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Bu tez, bir tuz ve yüzeyaktiflerin kendi kendine oluşumunu esas alan ve eriyik tuz yardımcı kendiliğinden oluşma (EYKO) yöntemi olarak tanımlanan yöntemle, mezogözenekli CdTiO₃ ince filmlerin sentezi ve karakterizasyonu üzerine odaklanmaktadır. EYKO yöntemi, mezogözenekli şeffaf ince filmlerin üretilmesi için uygun bir yöntemdir. Yakılmış edilmiş tozun ve jel numunelerinin karakterizasyonu x-ışını kırınımı (XRD), taramalı elektron mikroskobu (SEM), geçirimli elektron mikroskopisi (TEM), zayıflatılmış toplam yansıma (ATR-IR), azot adsorplama/desorplama ve polarize optik mikroskop (POM) teknikleri kullanılarak yapılmıştır.

İstenilen malzemenin hazırlanabilmesi için ilk adım; çözücü olarak etil alkolün kullanılmasıyla ve iki farklı yüzeyaktifle (bir üçblok kopolimer, P123, ve C₁₆H₃₃N(CH₃)₃Br, CTAB) birlikte, [Cd(H₂O)](NO₃)₂ tuzunun, titanya kaynağı olarak titanyum(IV)bütoksit'in (Ti(OC₄H₉)) ve titanyum alkoksidin hızlı polimerizasyonunu önlemek için asit olarak HNO₃'ün karıştırılmasıyla berrak bir çözeltinin oluşturulmasıdır.

Yüzeyaktiflerin hidrofilik alanlarının yönlendirilmesi ile hidrolize titanyum ürünleri ve eriyik tuz tarafından bir sıvı kristalin mezofazın oluşturulması için, hazırlanan berrak çözelti cam alttaş üzerine kaplandı. Jel numunelerinin yakılması ile, mezo-gözenekli CdTiO₃ materyali üretildi. Bu tez çalışması kapsamında, en uygun tuz:yüzeyaktif oranı, asit miktarı, yüzey aktif

madde oranı, kaplama yöntemi ve kalsinasyon rotasını belirlemek için çeşitli parametreler değiştirildi.

Daldırma ve çekme kaplama, döngülü kaplama ve dökme yöntemleri arasında daldırma ve çekerek kaplama yöntemi, daha az yan ürünle (ağırlıklı olarak CdO) malzeme üretmek için daha iyi sonuçlar verdi. Çözeltiye eklenen HNO_3 miktarı, hazırlanan jel filmlerin homojenliğini ve stabilitesini etkilemektedir. HNO_3 miktarının değiştirilmesinin yüzey alanını önemli ölçüde etkilememesine rağmen, aşırı miktarda asit ilavesiyle yakılmış filmlerde pürüzlü bir yüzeyin oluştuğu görüldü. CdTiO_3 350°C derecede nanokristalin yapıdadır ve 550°C dereceye kadar buyotlarını korumaktadır. Kalsinasyonu başlatma sıcaklığının, daha az yan ürünle istenilen malzemenin sentezlemesi için önemli bir parametre olduğu gözlemlendi. Mezogözenekli CdTiO_3 ince filmlerin, sentez koşullarına bağlı olarak 44 ile 79 m^2/g aralığında yüzey alanına ve 0.10 ile 0.16 cm^3/g aralığında gözenek hacmine sahip olduğu belirlendi.

Anahtar Kelimeler: CdTiO_3 , mezogözenekli ince filmler, eriyik tuz yardımcı kendiliğinden oluşma (EYKO).

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Chapter 1

Introduction

1.1 Porous materials

In the last decades, there are significant investigations on the synthesis of ordered porous materials by controlling structures and systematic tailoring pore architecture. Effective interactions of ions, atoms or molecules with both external surface and throughout the internal pore system of porous materials may enable advancements in wide range of fields, such as drug delivery, photonics, catalysis, separation, adsorption, and nano-devices [1], [2].

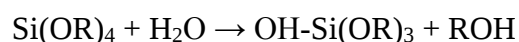
Pore-size, pore distribution and pore shapes in a material directly affect performance of the material in a specific application. Porous materials are classified as microporous (pore diameter $<2\text{nm}$), mesoporous (2-50 nm), and macroporous ($>50\text{ nm}$) materials [1].

Zeolites, which are aluminosilicates can be given as an example of microporous materials [3]. They are crystalline microporous materials with a large range of photochemical and catalytic properties. They are widely used as catalysts for petrochemistry, oil refining or especially when dealing with molecules having diameters below $10\text{ \AA}$ [4]. Also since the zeolites have complex channel structures, they present different shape selectivity. For example, a catalytic reaction can be directed to a desired side and undesired products can be avoided due to shape selectivity [4]. It was shown that besides the high electric field in the micropores, the electronic confinement of the guest molecules is responsible for pre-activation of the reactants [5], [6]. All of these properties mentioned about zeolites, which are very important in catalysis, ultimately depend on the thermal and hydrothermal stability of these materials. These properties of zeolites allow us to produce very stable materials, which are resistant to chemical attacks and heat. However, zeolites are inadequate when it is desired to work with reactants having larger dimensions than the pores. Therefore, scientists have turned their attention to increasing the pore size to a mesoporous region preserving the desired properties of the porous material mentioned above [4]. Especially working with larger molecules such as heavy oils or biomolecules, it has been shown that mesoporous materials can be used very efficiently in applications such as catalysis, energy storage, adsorption, separation, sensors,

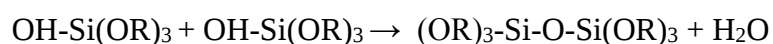
drug delivery and photonics at the scale of a few nanometers due to their high surface area. Microporous materials have been found to be inadequate to meet these specifications [1], [4]. These motivations trigger the proliferation of mesoporous materials. Pillared clays containing mesopores have been well studied [4], [7]. However, because of their disordered pore structure, it was shown that it was not easy for molecules to pass through the pores and they cause to coking in the catalytic processes. Also, it was shown, besides the disordered pore structure, they have a wide range of pore size that makes the diffusion process difficult to control. Since it has been shown that the ordered mesoporous materials show significant performance improvements in numerous applications, therefore significant studies have been carried out to synthesize ordered mesoporous materials with various compositions and morphologies. Enormous efforts have been made to explore the mechanism of mesostructure formation and explore their applications [2].

1.2. Sol-gel process

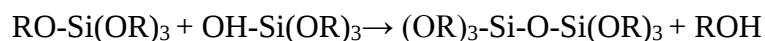
It is necessary to mention sol-gel process to understand the basis of this thesis work. Sol-gel is defined broadly as the method of preparing ceramic materials. In a sol-gel process, non-metallic and inorganic (thus including all metal oxides, nitrides and carbides) precursors undergo through the following steps; preparation of a sol, gelation of the sol, and removal of the solvent. The sol (colloidal suspension of solid particles in a liquid) may be produced from inorganic or organic precursors and may consist of dense oxide particles or polymeric clusters. The sol-gel process is based on hydrolysis and condensation/polymerization of the molecular precursors. Metal alkoxides are popular metal precursors since they can readily react with water. For example, hydrolysis reaction of a silicon alkoxide is as follows;



Depending on the amount of water present in the media, the reaction may go to completion (producing Si(OH)_4) or it may stop and when the metal precursor is partially hydrolyzed as shown above. Also, partially hydrolyzed molecules can link in condensation reaction;



or



This reaction can continue to form larger molecules by the process of polymerization [8].

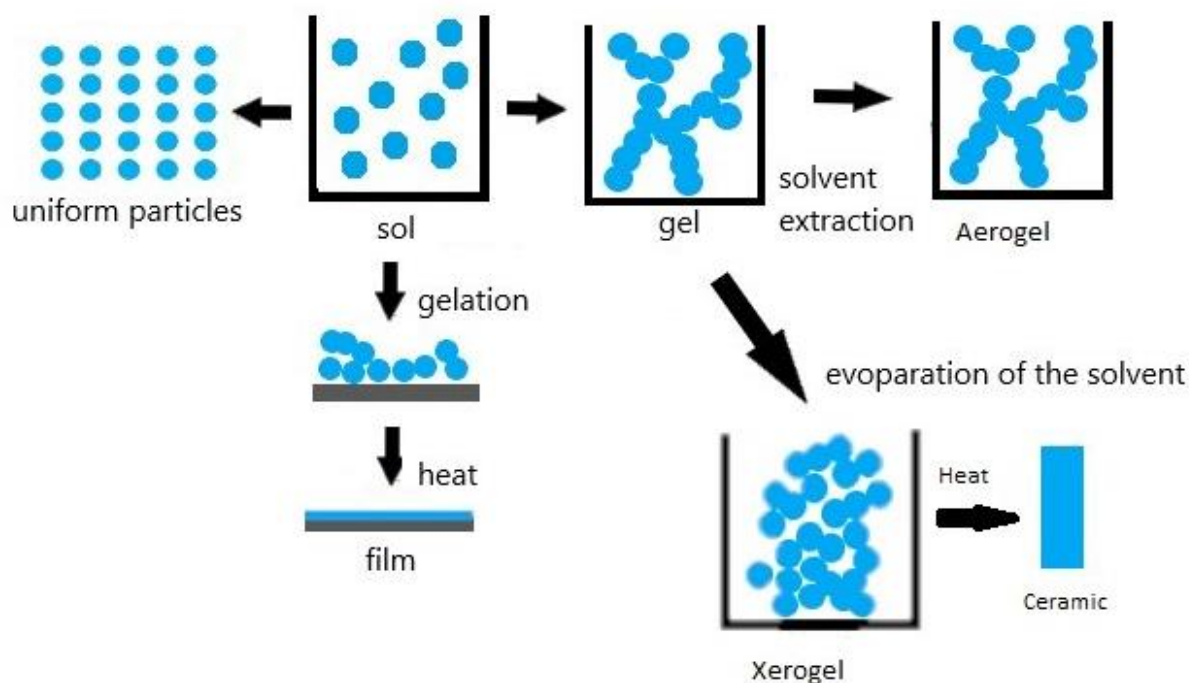


Figure 1. An overview of the sol-gel process.

The studies in sol-gel science can be divided into two groups in terms of the type of precursor used- silicates and non-silicates. For the synthesis of mesoporous materials, silica and aluminosilicates are two of the most widely studied compounds of the inorganic framework because of their tetra-connected covalent bonds. Since tetrahedral building blocks have a geometrical flexibility and exhibit a chemically stable property, their synthesis process is relatively facile compared to non-silicates. On the other hand, synthesis of non-silicates to produce mesoporous metal oxides have attracted attention since they have various and often unique properties, functions, and possible applications. [9].

Transition metal oxides are widely used in sol-gel process due to the presence of highly electronegative –OR groups that stabilize the metal in its highest oxidation state and render its sensitivity to a nucleophilic attack. However, several factors, listed below, distinguish the transition metal alkoxides from silicon alkoxides, which are the most commonly used precursor:

1) Since the transition metals have lower electronegativity, they are more electrophilic and thus less stable towards hydrolysis/condensation and nucleophilic reactions.

2) Transition metals generally have several stable coordination numbers. When they are coordinatively unsaturated, they can expand their coordination via oxalation, ololation or other nucleophilic association reaction.

3) To prepare homogenous gels rather than precipitates, studying with transition metal alkoxides requires a strict control of moisture due to their high reactivity.

4) Rapid kinetics of nucleophilic reactions of transition metal alkoxides are generally much more difficult to understand compared to silicates [8], [10].

One of the most important aspects of sol-gel processing is that, the fluid sol or solution is ideal for preparing thin films by common techniques like dip coating, spin coating or spray coating. Ability to control the pore structure (the pore volume, pore size, and surface area) of the coated film is one of the most important advantage of sol-gel processing. Thickness of the film and evaporation of the solvent from the gel, determines the porosity of the produced thin film since they directly affect the ongoing reactions (hydrolysis and condensation/polymerization) within the system. Unlike bulk gels, for the most film formation methods, the aggregation, gelation, and drying stages significantly overlap, establishing a time scale for aggregation or ordering, gelation and aging that depends on the evaporation rate of the solvent, generally water or ethanol [8].

1.3 Mesoporous materials

The first mesoporous material was obtained by using surfactants as a directing agent [11]. Surfactants molecules (a non-polar alkyl chain with a head group that can be neutral or charged and polar) come together and form micelles in a suitable solvent like water, depending on concentration. These micelles are comprising of typically 30-100 surfactant molecules depending on the size and density of the molecules. Increasing concentration of the micelles in an aqueous media may lead to lyotropic liquid crystalline mesophases. The mesophases can be observed as hexagonal, cubic-bicontinuous, cubic-spherical-micelles and lamellar [12]. The addition of a polymerizable additive (usually inorganic precursors) in the

medium of the micelles allows them to coalesce into a powder by coating and bringing the micelles together into a solid [11].

C. T. Kresge et al. synthesized first mesoporous silica by introducing the concept of liquid crystal templating mechanisms in which they used hexadecyltrimethylammonium chloride (CTAC) and silicate as polymerizing inorganic material. The hexadecyltrimethylammonium ions form micelle surfactant domains in an aqueous media. As-synthesized product was calcined at elevated temperatures to burn the surfactants to obtain mesoporous silica powders. They showed that in this mechanism inorganic material occupies the solvent region to form inorganic walls between the surfactant domains [13]. Later, the synthesis of mesoporous films was achieved by establishing various synthetic techniques. These techniques could be listed as liquid crystalline templating (LCT), evaporation induced self-assembly (EISA), molten-salt assisted self-assembly (MASA), and hard templating (HT) methods.

1.3.1 LCT

It was shown that many surfactants form lyotropic liquid crystalline (LLC) mesophase with solvents (generally water) at high concentrations and most of the lyotropic liquid crystals consist of close packed and ordered micelles [14]. In mesoporous silica, silica forms the pore walls. In LLC, these units are consisting of polar parts of the surfactant and water, called hydrophilic domains in the mesophase [12]. Various polymerization reactions can be performed in hydrophilic units to obtain solid mesostructures [15], [16], [17], [18]. In 1995, G. S. Attard *et al.* synthesized mesostructured silica as a thin film from a liquid crystalline mesophase. This was a significant step up in the field to understand the formation mechanism of mesostructured silica. It was shown that when all the reactants were put together, a liquid crystalline mesophase is formed and polymerizing silica source in this medium turns into a solid material while preserving the structure of the liquid crystalline mesophase. By this way it was shown that liquid crystalline phase can direct an inorganic reaction and this work is one the first studies of production of mesoporous thin films [19]. Mesoporous materials such as SiO₂ [19], TiO₂ [20], CdS [15], [16], [17], [18] were synthesized by LCT method. In these syntheses, water-surfactant-salt LLC mixtures were used in very low salt concentrations. Therefore, the materials obtained are both small in size, and poor quantity [15], [16], [17], [18], [21], [22].

1.3.2 EISA

Another significant work was conducted by F. C. Brinker *et al.* in 1999, in which a new and practical method of producing mesostructured thin films was introduced- called evaporation-induced self-assembly (EISA) [23]. This method was first used to synthesize mesoporous silica films. A homogeneous solution prepared with a silica precursor, surfactant and solvent is coated to a substrate by spin or dip coating method. It was shown that increasing surfactant concentration drives self assembly, which was defined as a spontaneous organization of substances due to non-covalent interaction with no external force. Silica-surfactant micelles organize into a highly oriented liquid crystalline mesophases. By a gradual evaporation of the solvent and template elimination, ordered mesoporous films are produced.

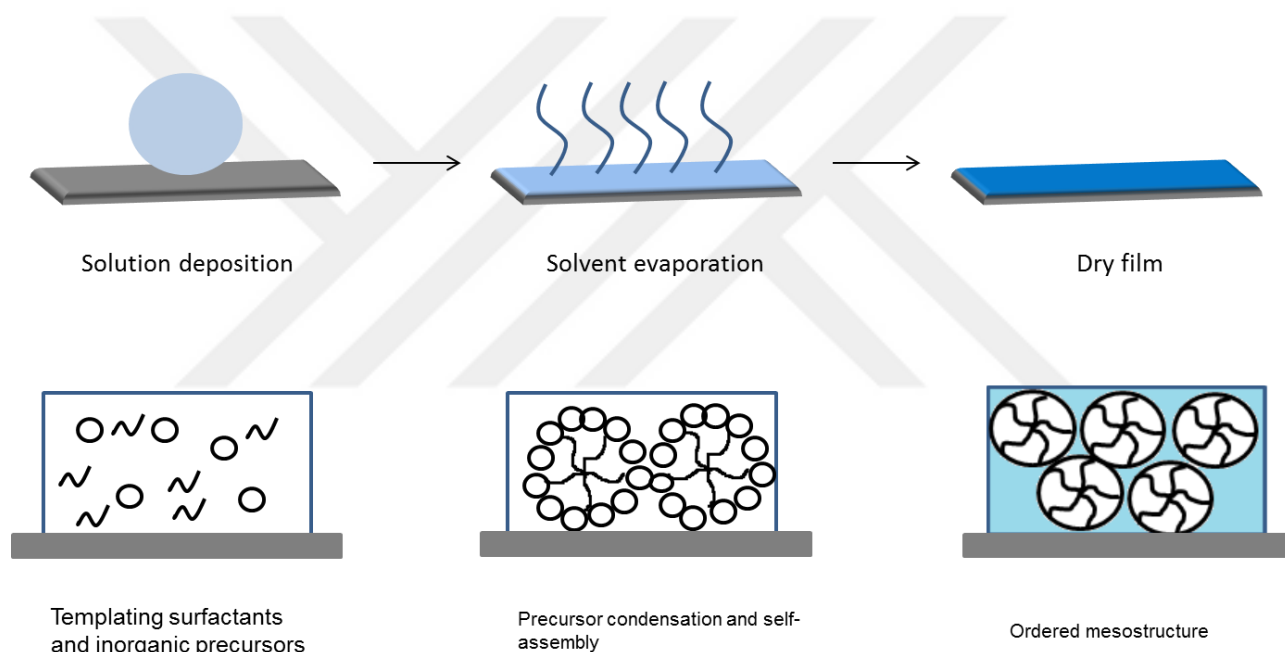


Figure 2. Schematic representation of a typical EISA process for mesoporous materials. The top sequence shows the synthesis procedure. The self-assembly process of mesostructure is shown at the bottom sequence.

It was found that the mesostructures are formed in the last stage of the solvent evaporation. In this method, solvent has to wet the substrate effectively and it should be volatile. During this process methanol, ethanol, or tetrahydrofuran are generally used as solvents, which have weak polarities. Since hydrophilic and hydrophobic parts of the surfactants can interact with the solvent when it has a weak polarity, the surfactant loses its hydrophilic or hydrophobic

properties. Thus, in the starting solution the self-assembly of the surfactants can be prevented. In this regard, the assembly can be only induced upon the solvent evaporation [2, 24]. In this process the solvent that guide and preserve the formation of the mesostructure is volatile and when it evaporates the mesostructured semisolid may be disrupted.

By using EISA method, *Deng et al.* synthesized highly ordered mesoporous carbons and silicas with large accessible pores by using PEO-b-PS (poly(ethylene oxide)-b-polystyrene) copolymer as surfactant template [25]. In the study, resols was used as carbon precursor and tetraethyl orthosilicate (TEOS) was used as silica precursor. Obtained mesoporous carbon material has a pore size of ~ 23 nm, and high BET surface area of around ~ 1510 m²g⁻¹ and pore volume of 0.95 cm³g⁻¹, with a large contribution from the micropores. The large pores with different components in walls, such as silica, and carbon are attractive for various applications including catalysis, electrode materials, and adsorption.

Formation mechanism of EISA was systematically investigated by *Sanchez et al.* and the synthesis of highly organized mesoporous yttria-zirconia and ceria-zirconia thin films were demonstrated for the first time by using EISA method. Cubic or 2D hexagonal mesophases were obtained depending on the amount of water added to the system [26].

1.3.3 Hard templating

Compared to silicon alkoxides, it is more difficult to control the polymerization and hydrolysis of transition metal alkoxides. Thus, after removal of the surfactant domains, the synthesized metal oxides usually show a disordered structure and low thermal stability [27]. As an alternative technique, hard templating method was developed by *Ryoo et al.* in 1999 [28]. In this method, pre-prepared mesostructured material (especially mesoporous silica) is calcined and a porous material is obtained. The pores are then filled with impregnation of solutions of various metal salts and calcined at high temperatures to obtain metal oxides [27], [28], [29]. In soft templating methods, when the template has a low decomposition temperature, the material obtained using by this method can be amorphous. However, it was found that by using hard templating method crystalline mesoporous materials can be obtained [27], [30], [31]. Upon removal of the hard template, silica, by chemical etching, ordered metal oxides are obtained. With hard templating, however, it was shown that, since metal ions cannot be homogeneously fill the mesopores, metal oxides do not have a homogeneous

distribution on the inner surface of the silica. New methods needed to be developed in order to cover the inner surfaces with a homogeneous and desired thickness.

The first nanostructured metal oxide was synthesized by *Zhu et al.* using hard templating method [9,32]. Porous Cr_2O_3 was synthesized by aminosilylation of the surface silanols of the template, SBA-15, which is a material having amorphous silica walls and hexagonally arranged straight channels (prepared using pluronic P123, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, as a templating surfactant). The obtained material has reversed 2-D hexagonal structure formed by nanorod arrays having a diameter of 8 nm. The BET surface area of the obtained Cr_2O_3 material is $58.1 \text{ m}^2\text{g}^{-1}$. By the nanocasting method using mesoporous silica or carbon as hard templates, various mesoporous metal oxides were synthesized, such as TiO_2 , Al_2O_3 , CuO , Ga_2O_3 , MnO_2 , RuO_2 , ZrO_2 , MgO , CoO , SnO_2 , ZnO , and Fe_3O_4 [32,35,36].

1.3.4 Molten-Salt Assisted Self-Assembly (MASA)

As mentioned above, many surfactant molecules form a LLC phase in aqueous media. For instance, it was shown that a LLC phase can be obtained by using only a non-ionic surfactant and a transition metal nitrate hexahydrate salt [35]. In this system, the water molecules in the metal aqua complex and counter anions are coordinated with the metal ions. To form LLC mesophases, the metal ions interact with the ethoxy groups of the surfactant molecules via hydrogen bonding through water molecules, coordinated to a metal center in salt- $\text{C}_{12}\text{EO}_{10}$ (denoted as S-EO and $\text{C}_{12}\text{EO}_{10}$ is $\text{C}_{12}\text{H}_{25}-(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$) mesophases [35], [36], [37]. However, if the metal ion coordinates with the ethoxy group of the surfactant, they form a complex and crystallize as a solid product [37]. Besides S-EO system, water-salt-surfactant (W-S-EO) systems were also investigated. Compared to W-S-EO system, S-EO mesophases are found to be more stable. It was seen that addition of salt species to the water-surfactant mesophase destroys the mesophase at around a 20 w/w% (weight of salt/total weight) salt concentration, whereas the mesophase can exist up to 70 w/w% in S-EO systems [38]. Later studies showed that by adding a charged surfactant (cetyltrimethylammonium bromide, CTAB) into the media, metal ion/ $\text{C}_{12}\text{EO}_{10}$ mole ratio can be increased to a record high metal ion concentration in the LLC phase. Interaction of the charged hydrophilic and hydrophobic domains of assembled two surfactants with metal salt species in the mesophase, stabilizes

structure of the mesophase and increase the salt uptake of the LLC mesophase [39]. In 2011, the $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ - $\text{C}_{12}\text{EO}_{10}$ system was investigated and it was shown that salt species are in the molten phase and act as a solvent in the salt-surfactant LLC mesophases [39]. Since there is a confined space between the surfactant domains, due to the soft confinement effect (SCE) the melting point of the salt decreases drastically and molten salt does not crystallize even at very low temperatures [38], [39], [40].

In 2013, *Dag et al.* introduced a new synthesis method called molten-salt assisted self-assembly (MASA) to produce metal oxide-silica and metal titanate thin films [41]. In this system two solvents (molten metal salt and ethanol or water) and two surfactants (CTAB as a charged surfactant and $\text{C}_{12}\text{EO}_{10}$ as a non-ionic surfactant) were used to form the mesostructure. Volatile solvent (ethanol or water) is used to dissolve the ingredients to obtain a homogenous solution. The non-volatile solvent- molten salt, does not evaporate at even high temperatures and keeps the mesophase stable during calcination step. By FTIR spectra of fresh films, it was shown that in the LLC phase, the titania species and molten salt form a stable solution and even at high salt concentrations (higher than solubility limits of salt in water) salt species stay in the liquid phase due to SCE. It was shown in the titania system that metal salt slowly reacts with the pre-formed amorphous titania walls, among the surfactant domains to form metal titanate upon calcination. After coating and calcination steps, sponge like mesoporous metal titanate was obtained, which is stable up to 450-500°C and collapses to form a crystalline bulk metal titanate above this temperature.

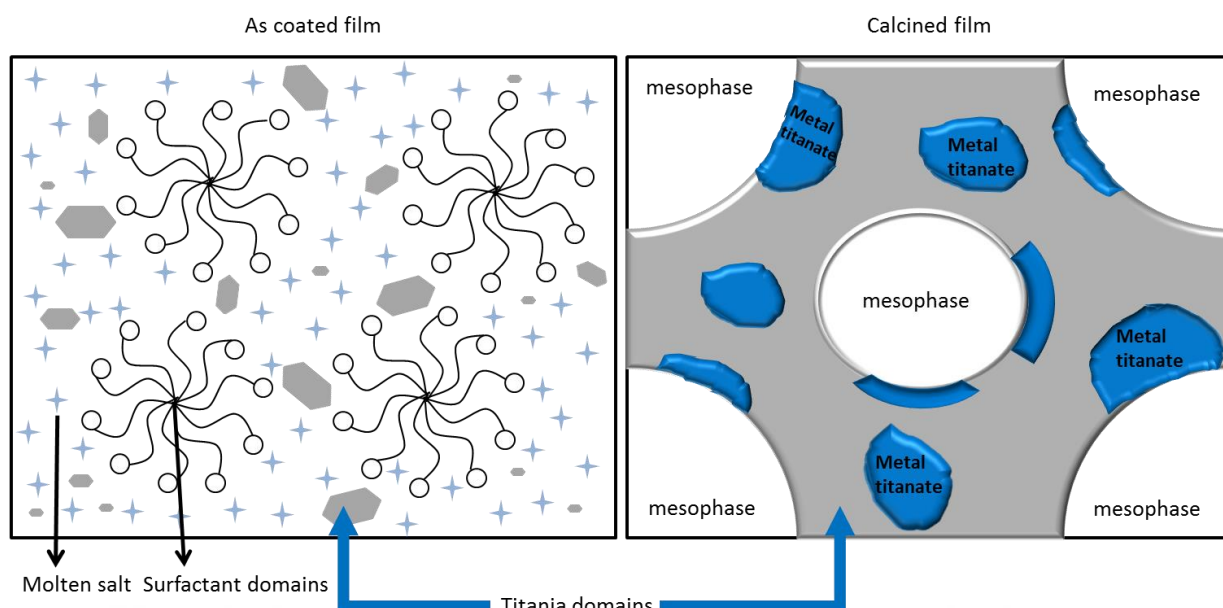


Figure 3. Illustration of meso-domains of the as-coated (left) and calcined thin films (right) from a MASA process.

In this method, the fact that the primary solvent is the molten salt, which does not evaporate during assembly and calcinations processes is an advantage. The solvent that guide and preserve the mesostructure is not volatile. This property of MASA system, distinguishes it from EISA process, in which evaporation of the solvent disrupts the mesophase.

Mesoporous CdTiO_3 thin films were synthesized by using MASA method by Dağ's group [41]. In the scope of that work, CTAB and $\text{C}_{12}\text{EO}_{10}$ were used as surfactants in order to synthesize the material in the assembly process. $[\text{Cd}(\text{H}_2\text{O})_4](\text{NO}_3)_2$ was added to the system as salt species and titanium (IV) butoxide was used as the inorganic polymerizing substance. It was seen that mesoporous CdTiO_3 samples are stable up to 550°C and above this temperature the material collapse and undergo a phase change into a crystalline bulk phase. In the scope of this thesis work, in place of $\text{C}_{12}\text{EO}_{10}$, P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, EO is ethylene oxide, PO is propylene oxide units) was used as the nonionic surfactant. Compared to $\text{C}_{12}\text{EO}_{10}$, P123 may provide larger pores and better crystalline pore walls, which is, may be, beneficial for some applications, when discharging and charging of the produced materials [42].

Chapter 2

2. Experimental Procedure

2.1. General route for synthesis of thin films

2.1.1. Materials

Two different surfactants are used in this thesis work; P123 (a triblock copolymer with an average molecular weight of $\sim 5,800$ g/mol) and CTAB ($\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Br}$ with a molecular weight of 364.45 g/mol). Titanium(IV)butoxide ($\text{Ti}(\text{OC}_4\text{H}_9)_4$, 97% Sigma-Aldrich) is used as titania precursor and cadmium nitrate tetrahydrate ($[\text{Cd}(\text{H}_2\text{O})](\text{NO}_3)_2$, 99% Sigma-Aldrich) is used as metal salt. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 99.8% Sigma-Aldrich) and nitric acid (HNO_3 , 65% Sigma-Aldrich) are used as solvent and acid, respectively.

2.1.2. Preparing the clear solutions

Firstly, a clear solution of the ingredients should be prepared. Dissolve both surfactants (0.0527 g CTAB and 0.1978 g P123) and a desired amount of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 2.5 ml ethanol. Stir the solution for 24 hours. Then add the required amount of HNO_3 (depends on the concentration of the metal salt, see Table 1) to the solution and stir for 5 minutes. Finally, add titanium(IV)butoxide to the mixture and stir for another 5 minutes. In this work, two ratios were kept constant; CTAB:P123 ratio at 5:1, and Ti:Cd ratio at 1:1. By this way the size and amount of surfactant domains are kept constant to observe the effect and the changes in the liquid phase between the surfactant domains. Also, molar ratio of the metal salt and titania was kept constant to obtain stoichiometric compound, CdTiO_3 . Accordingly, the clear solutions of the compositions in Table 1 were prepared.

Mole ratios of chemicals			The amounts of chemicals (g)					
Cd/Ti	CTAB/P123	Cd/P123	Ti(OBu) ₄	P123	CTAB	Cd Salt	Acid	Ethanol (ml)
1	5	10	0.0985	0.1678	0.0527	0.0893	0.2	2.5
1	5	20	0.197	0.1678	0.0527	0.1785	0.4	2.5
1	5	30	0.2955	0.1678	0.0527	0.2678	0.6	2.5
1	5	40	0.394	0.1678	0.0527	0.3571	0.8	2.5
1	5	50	0.4925	0.1678	0.0527	0.4464	1	2.5
1	5	60	0.591	0.1678	0.0527	0.5356	1.2	2.5
1	5	70	0.6895	0.1678	0.0527	0.6249	1.4	2.5
1	5	80	0.788	0.1678	0.0527	0.7142	1.6	2.5
1	5	90	0.8865	0.1678	0.0527	0.8035	1.8	2.5
1	5	100	0.985	0.1678	0.0527	0.8928	2	2.5

Table 1. The amounts of substances used in the preparation of CdTiO₃.

2.1.3. Preparation of fresh thin films

Spin coating, dip coating and drop casting methods were used to coat the glass substrates. For spin coating method, put 1 ml of the prepared clear solution on a glass substrate over the spin coater and spin it at 1000 rpm for 20 seconds. For drop casting method, put around 1 ml of the solution on to a glass substrate, skim the excess with a clean spatula and spread the mixture to cover the entire upper surface of the glass. Finally, for dip coating method, immerse the substrate into the prepared solution at a constant speed of 0.45 cm/sec and coat the glass

substrate. Then pull the glass substrate upward at the same constant speed as excess solution is draining from the surface.

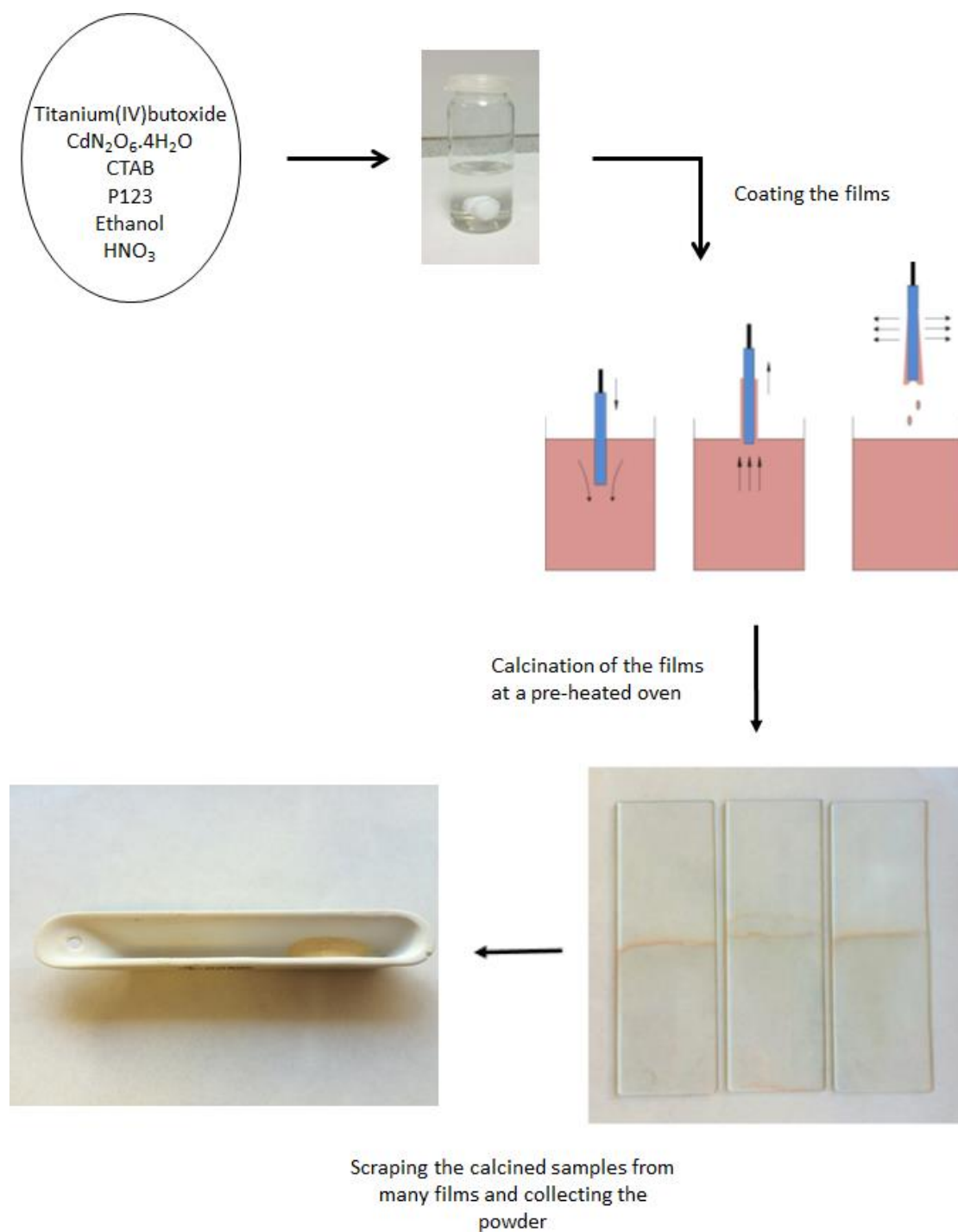


Figure 4. Preparation of mesoporous CdTiO_3 powder.

2.1.4. Calcination and fabrication of mesostructured CdTiO₃ thin films

After preparing fresh films, insert the gel-like samples immediately into a preheated oven and calcine them from 150°C to 350°C by 1°C/min increments (can be annealed at various temperatures). After heating to 350°C, calcine the films at this temperature for 30 minutes. Remove the films after cooling the oven slowly. Do not expose the films to a consecutive temperature change by opening the lid over and over again during putting all the films to the oven.

2.1.5. Scraping the films

After the calcination step, let the films cool down slowly in the oven. Then take off the films out of the oven for collecting as a powder. Scrape the films slowly to collect powder for several measurements. Scrape many films until adequate amount of powder is collected for analysis.

2.2. General Optimizations

2.2.1 Optimization of salt ratio

Optimizations have been done to determine the optimum metal salt to surfactant ratio. Both fresh films and calcined films were observed to determine the optimum metal salt to surfactant ratio. To determine the optimum salt amount for the system, different amounts of metal salt were added to the solution to change Cd(II) salt to P123 ratio (10-100:1). Fresh films are examined by collecting POM images, XRD patterns and IR spectra. Also, XRD, IR, N₂ sorption, Raman and SEM measurements were done for the calcined and collected powders.

2.2.2. Optimization of acid amount

Optimizations have been done for the concentrated nitric acid (HNO_3), which prevents quick polymerization of titanium alkoxide to enhance the interaction of metal and titania to form metal titanates and also helps to solve the metal salt in the solution. For 50 mol ratio of salt to P123, for example; 0.5 g, 1 g and 1.5 g of concentrated HNO_3 was added to the mixture and concentration of the solution was kept constant to find out the optimum pH for the solution.

2.2.3 Coating technique

Spin coating, dip coating and drop casting methods were employed to coat the glass substrates. In this study, dip coating method were mainly used since it seems to work better as going to be discussed later. The optimum thickness for a film sample is that the gel film has enough thickness that the solvent evaporation is efficient and the produced film after calcination is not too thin that it will not take too much time to produce sufficient powder for further measurement.

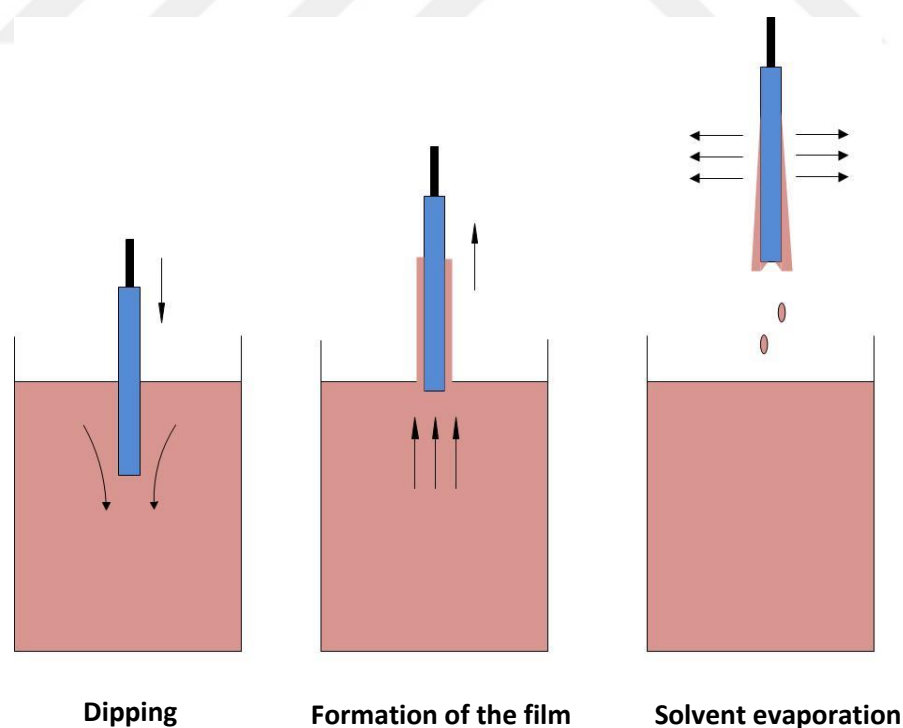


Figure 5. The schematic representation of a dip coating process.

2.3. Instrumentation

2.3.1. XRD Diffraction

XRD measurements were done by using a Rigaku Miniflex diffractometer, which uses a high power Cu-K α source operating at 30 kV/15 mA and generates x-rays with a wavelength of 1.5405 Å. The samples were prepared on glass microscope slides by various methods. At small angles, measurements were done between 1° and 5°, 2 θ range with a 1°/min scan rate. At high angles measurements are done between 20° and 80°, 2 θ range with a 1°/min scan rate.

2.3.2. ATR Spectra

A Bruker Alpha Platinum ATR (Attenuated Total Reflectance) spectrometer was used for ATR-IR spectra. The measurements were done by adding a few drops of the prepared solution on the diamond ATR crystal, with a resolution of 4 cm⁻¹ and 64 scans in the 400-4000 cm⁻¹ range.

2.3.3. SEM Imaging and EDX Analysis

SEM images were recorded by using FEI-Quanta 200 FEG ESEM. Samples to be imaged were coated on silicon wafers. Silicon wafers were attached to aluminum sample holders with conducting adhesive tabs.

2.3.4. TEM imaging

For TEM images a FEI Technai G2, operating at 200 kV was used. After scraping the calcined thin film samples, a tiny amount of the collected powder was dispersed in 5 ml of

ethanol for 30 minutes. Then the dispersed solution was put on a holey carbon film on 200 mesh copper grids and heated under light to evaporate ethanol.

2.3.5. Polarized Optical Microscope (POM)

POM images were obtained by using a ZEISS Axio Scope A1 polarizing optical microscope in transmittance mode. Temperature controlled measurements were done by using a Linkam LTS350 temperature controlling stage attached to the microscope and a LinkamT95-LinkPad temperature programmer attached to the stage. The samples to be analyzed were coated on glass microscope slides.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Investigations on fresh films

3.1.1. Determination of salt uptake of LLC phase

As introduced before, MASA is a method that two different surfactants assemble to form LLC mesophase with the help of two solvents one of which is the molten salt. This is a very sensitive process, where the molten salt and hydrolyzed titania are guided by micella building blocks. In this thesis work, mesoporous CdTiO_3 thin films were prepared by using the MASA method by optimizing the reaction conditions. Interaction of the charged hydrophilic and hydrophobic domains of assembled two surfactants with metal salt species in the mesophase, stabilizes the structure and increases the salt uptake of the LLC mesophase. One of the remarkable aspects of MASA synthesis is that; due to SCE, the melting point of the salt decreases drastically and molten salt does not crystallize even at very low temperatures and the formed LLC mesophase is quite stable over time [39]. However, there are some parameters to be optimized in order to maintain the LLC mesophase for long periods, otherwise salt may leach out to form bulk salt crystals on top of the film. One of these parameters is the amount of salt needed to maintain the LLC phase stability. As the more salt is added to the system, the thicker CdTiO_3 walls could be obtained. Because the layer formed by molten salt and titania precursor would get thicker, see **Figure 6**. As mentioned before, the interaction of the charged hydrophilic and hydrophobic domains of assembled two surfactants with metal salt species is a driving force for LLC formation. Therefore, concentration of surfactant molecules with respect to molten salt is a very crucial parameter in terms of phase stability. For example, when more liquid is added between the surfactant domains, the attractive forces start to weaken and stability of the mesophase would be deteriorated at some

point and salt species would leach out and start grow out of the mesophase to form undesired bulk salt crystals, see **Figure 6**.

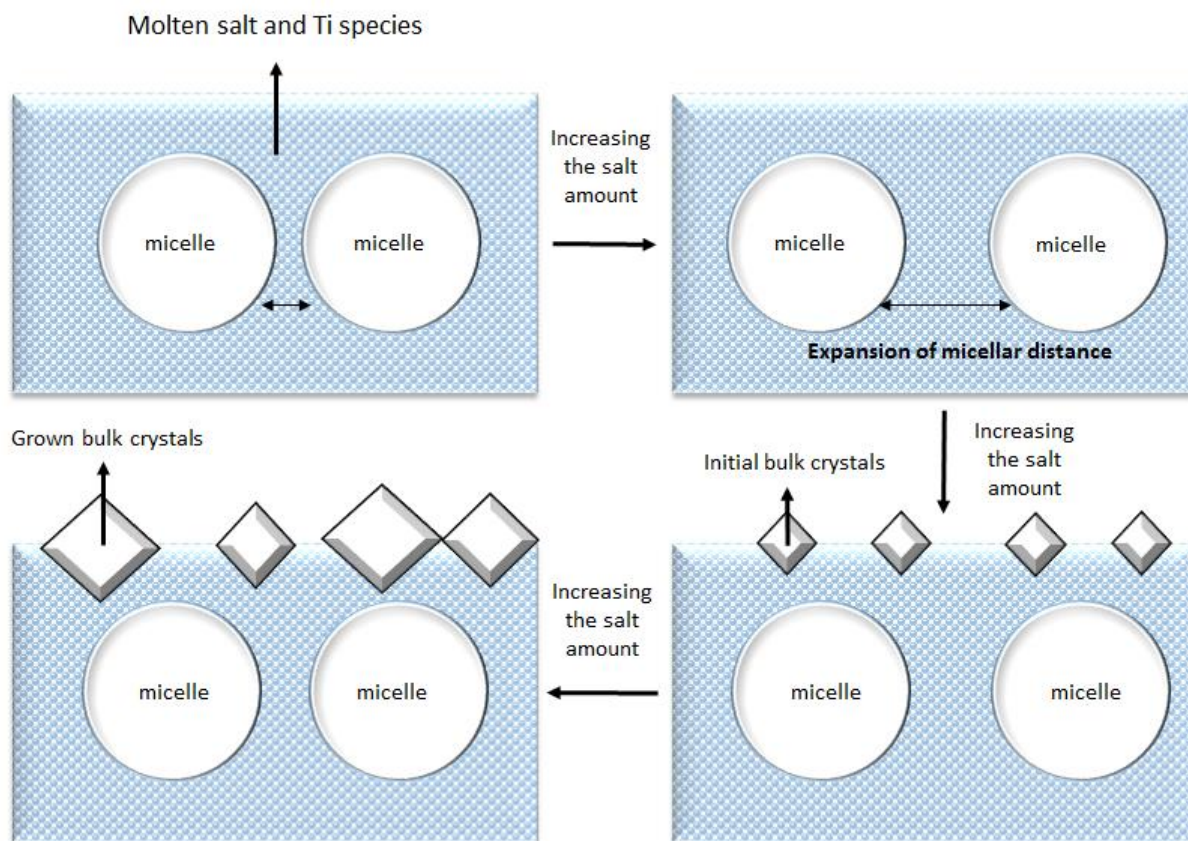


Figure 6. Behaviour of the mesophase when the salt:surfactant ratio is increased.

To form a stable metal titanate solid network, it is important to obtain an ordered mesophase at an early stage of film preparation to have a good groundwork for later stages. Homogeneously dispersed surfactant domains surrounded by homogeneously dispersed molten metal salt and titanium species is an ideal place to start building a mesoporous structure having a homogeneously distributed pore size and high surface area. Therefore, a detailed analysis of fresh samples is important in order to initiate the process in a right way and to understand/control the formation of the porous structure at later stages.

The experiments were carried out by increasing the salt content of the system. Small angle XRD is a powerful tool to investigate the LC order and also the order of the mesostructure.

Although the intensity of XRD lines can be misleading to comment on the meso-order, if the measurement is supported by analyzing many samples and if they are all held in the same conditions, the line intensities can be compared to comment on the meso-order. In this work, while comparing the XRD patterns of fresh samples, all the films had similar thicknesses and were produced under the same conditions. The changes by using 8 as-prepared thin film samples with different salt:P123 ratios were examined. **Figure 7** shows the small angle XRD patterns of the as-prepared thin film samples, prepared by using increasing salt:surfactant mole ratios.

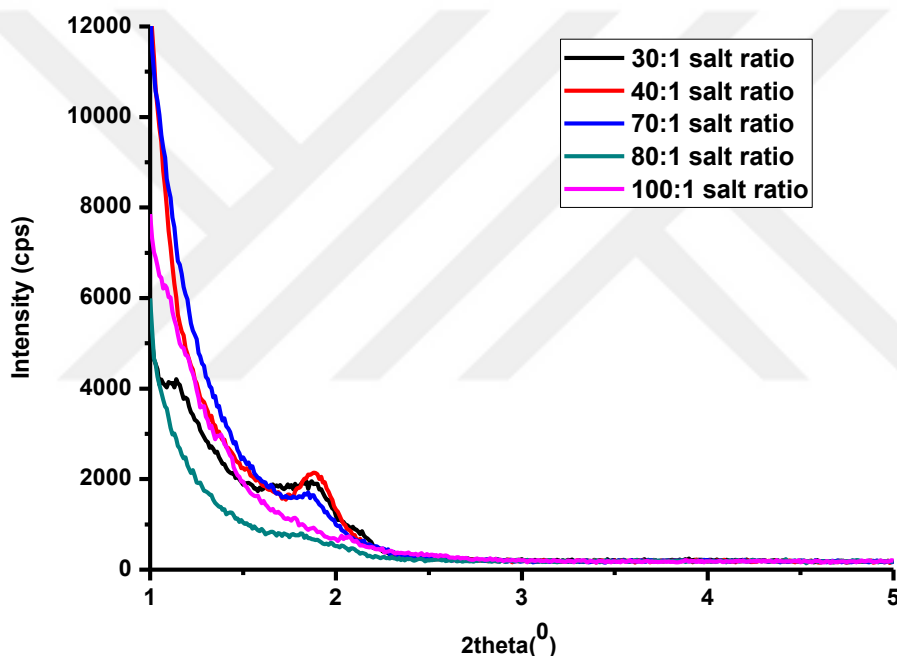


Figure 7. Small angle XRD patterns of the as-prepared thin film samples, prepared by different salt:surfactant mole ratios (as indicated in the patterns).

Since the formed mesophase displays the most intense line at an angle smaller than 1° , 2θ , the intensity change cannot be examined by small angle XRD pattern of the sample using our diffractometer. The effect of increasing the salt:surfactant mole ratio could not be observed clearly, since the intensity of the second line is not sufficient to comment on this matter. However, the diffraction line at **Figure 7** began to disappear as the salt:surfactant mole ratio

was increased. As the last sample containing 100 salt:surfactant ratio did not diffract at small angles, it was assumed that the mesophase formed at this composition is disordered. To determine the salt uptake of the films, further investigations were done by calcining the samples and monitoring using SEM, N₂ sorption (adsorption-desorption), and XRD techniques.

3.1.2 Determination of surfactant amount

As mentioned before, salt uptake of the LLC media can be enhanced by adding a charged surfactant to the media that may be necessary to produce stable mesoporous materials with some salts as precursors [38]. Since, the salt uptake of the LLC media correlates with the amount of charged surfactant in the media it is important to find the optimum CTAB/P123 and salt:surfactant ratio. The idea is to use the minimum amount of surfactant necessary to produce a well-defined mesoporous film, while determining the effect of each component on the self-assembly process (**Figure 8**).

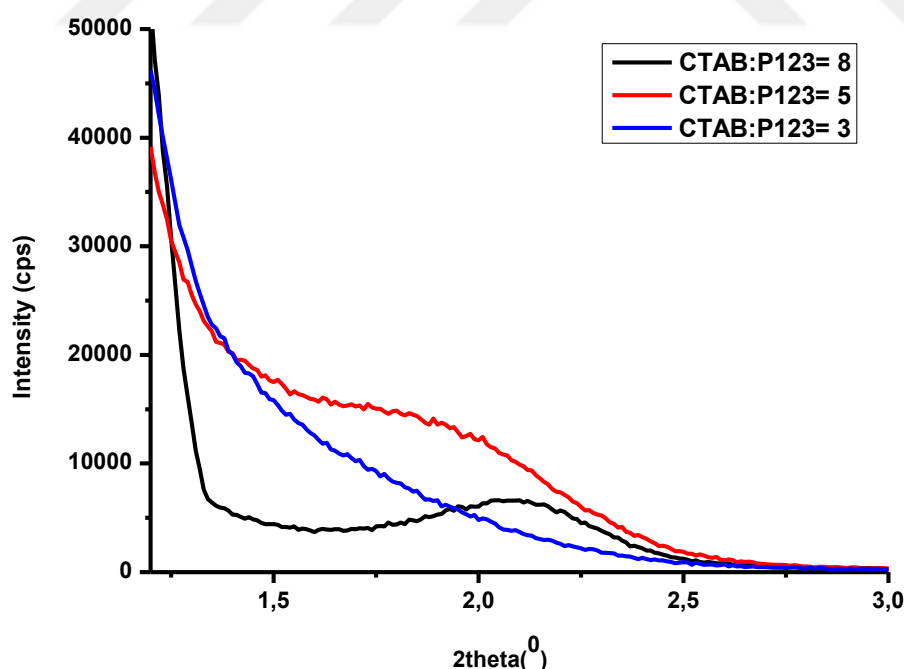


Figure 8. Small-angle XRD patterns of the fresh samples by increasing CTAB/P123 molar ratio of 3, 5, 8 using 50 salt/P123 ratio.

As shown in the small-angle XRD pattern of a sample with 50 salt:P123 ratio, the CTAB/P123 molar ratio of 3 does not seem to have a meso-order, whereas as the CTAB/P123 ratio is increased to 5 and 8, the films shows an ordered structure. As mentioned before, since the idea is to use the minimum amount of surfactant necessary to form an ordered mesophase and there is no much difference between the XRD patterns of 5 and 8 ratio, 5 CTAB/P123 ratio was chosen for further investigations.

3.1.3 Stability of fresh films

Maintaining the LLC phase stable for long periods of time is a challenge. For some applications, the period before the salt starts to crystallize can be too short. Therefore, it is important to determine the stability of LLC phase over time. The effects of aging on fresh films were observed at high angles (**Figure 9**).

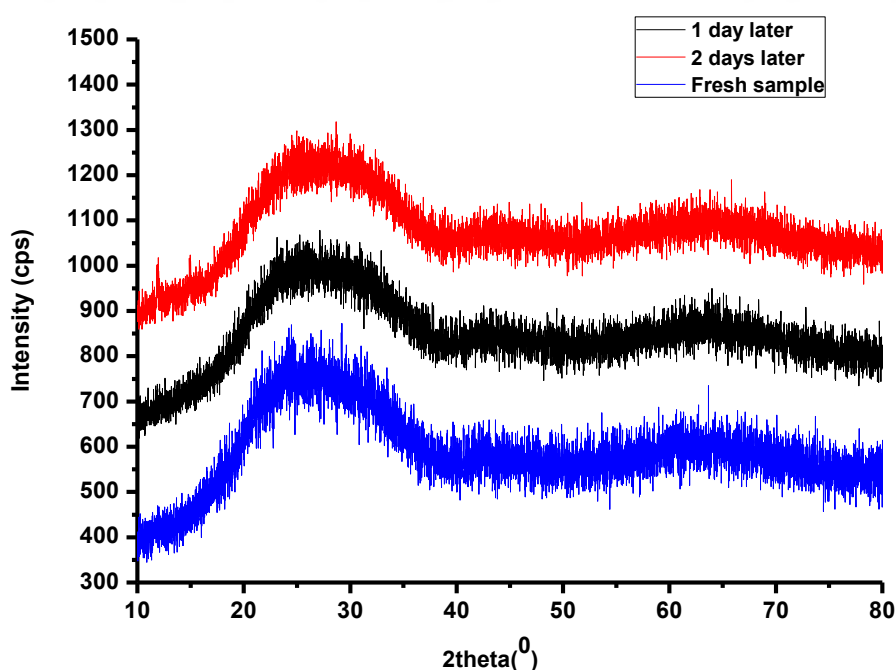


Figure 9. Time dependent XRD patterns of 80:1 salt:P123 ratio (as shown in the patterns).

Firstly, it is expected that a pure LLC phase will not exhibit a crystalline order at the atomic level. No diffraction line should be observed as it should exhibit amorphous properties. In order to determine the stability of the as-prepared samples over time, a sample with 80:1 salt:P123 ratio was prepared and followed by recording their small angle XRD patterns over time (see **Figure 9**). **Figure 9** shows that even at very high salt:surfactant ratios, the LLC mesophase can keep the salt between the surfactant domains for a long time, which is an extraordinary property. The fact that, salt or CTAB crystals does not leach out even after 2 days, indicates the mesophase is stable long enough for further heat treatments and may be advantageous for many other applications.

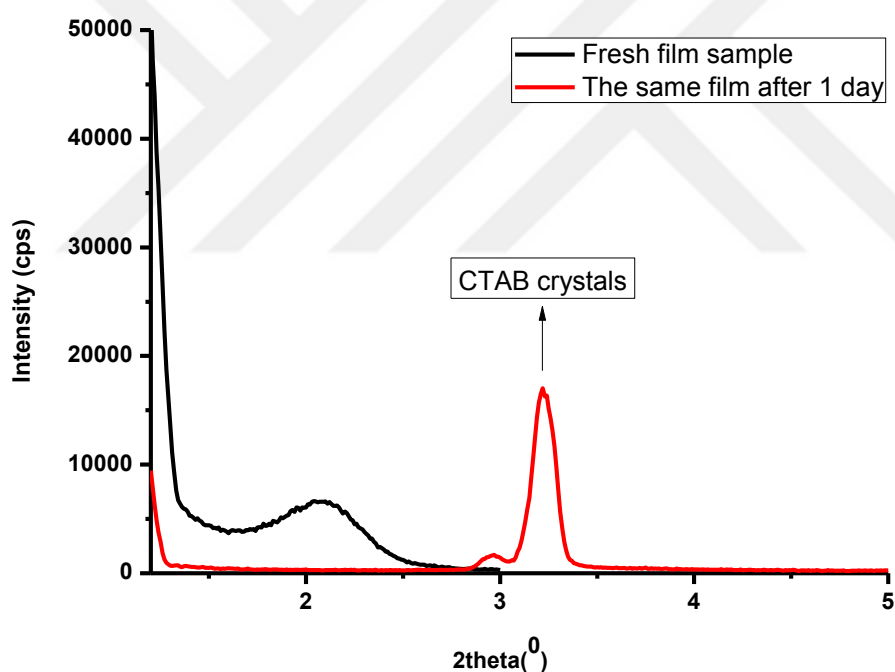


Figure 10. The small angle XRD pattern of a fresh film containing 50 salt:surfactant mole ratio and 8 CTAB:P123 mole ratio.

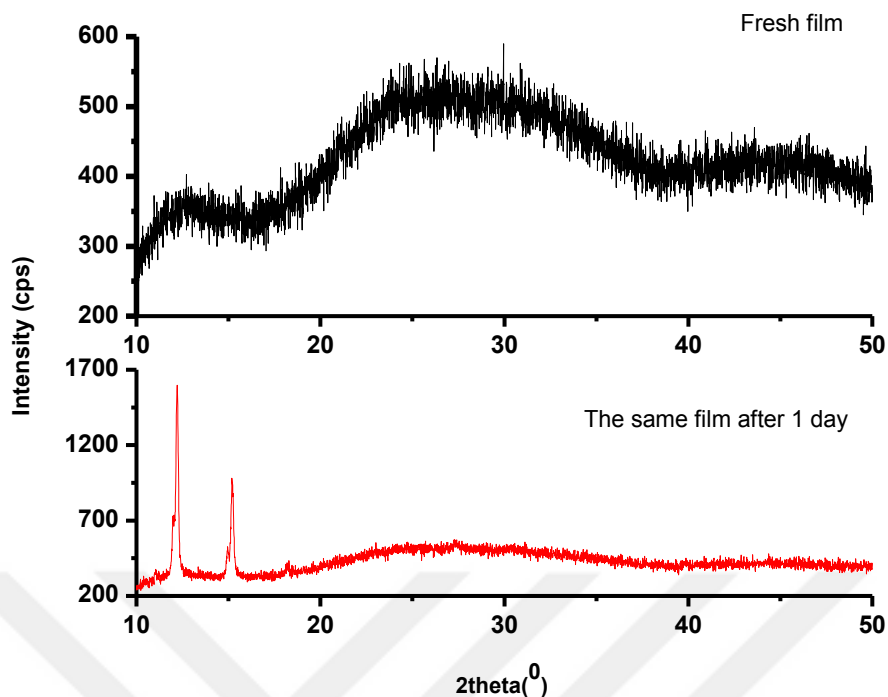


Figure 11. The high angle XRD pattern of a fresh film containing 50 salt:surfactant mole ratio and 8 CTAB:P123 mole ratio.

Figures 10 and 11 show how the fresh films behave after aging. The films leached out salt and CTAB crystals after 1-day aging in the gel-phase. The sharp diffraction lines over 3° , 2θ , originates from charge surfactant crystals and the high angle sharp lines are from the salt crystals.

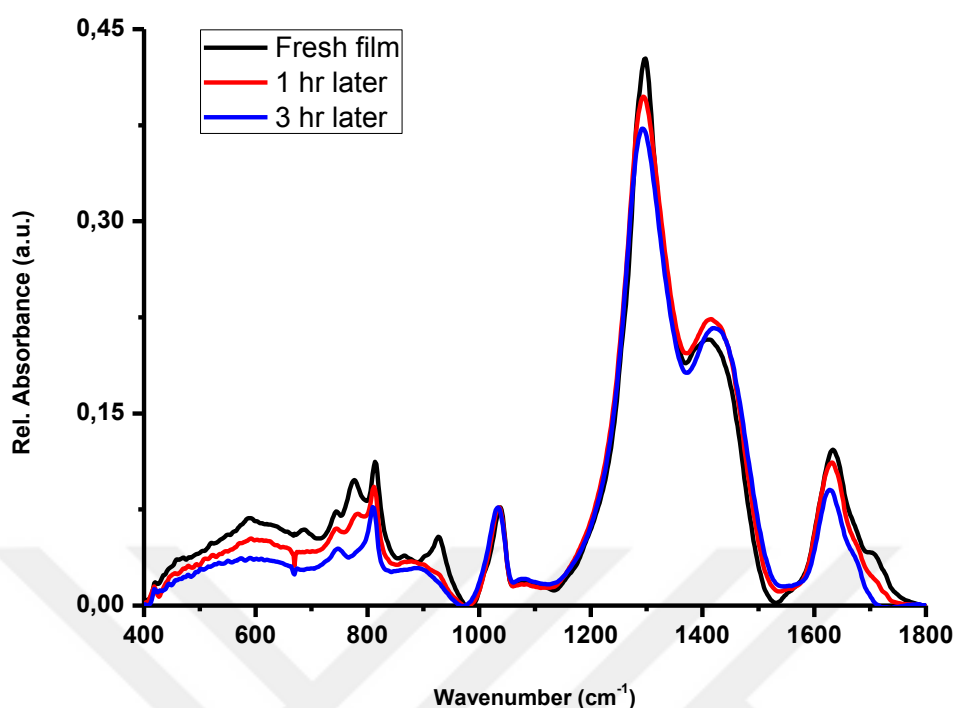
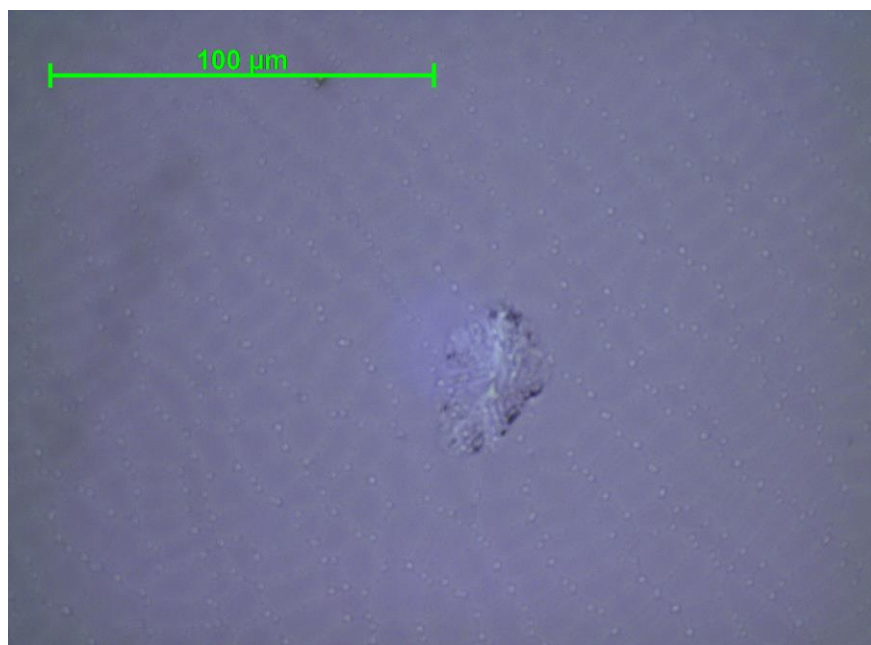


Figure 12. ATR-IR spectra of fresh sample, 1hour aged sample and 3 hours aged sample.

As mentioned before, the addition of concentrated HNO_3 acid stabilizes the mesophase by slowing down the condensation process of titania species. The IR peaks at 1293 and 1413cm^{-1} are due to nitrate ions coordinated to Cd(II) ions in the media and the peak intensity decreases by aging time (see **Figure 12**). The peak intensity due to water (at around 1620 cm^{-1}) decreases with time because of the coordination of nitrate ions to the metal ions. This is evidenced from the change on the nitrate asymmetric stretching region ($1250\text{-}1500\text{ cm}^{-1}$) in the spectra in Figure 12. Overall, the salt species are in the molten phase and solvates the titania species to keep them in the mesophase.

The XRD patterns of the fresh samples show that there has been crystallization after some time period, **Figure 11**. Bulk crystals have formed on top of the film that can also be detected by POM (see **Figure 13**).

A)



B)

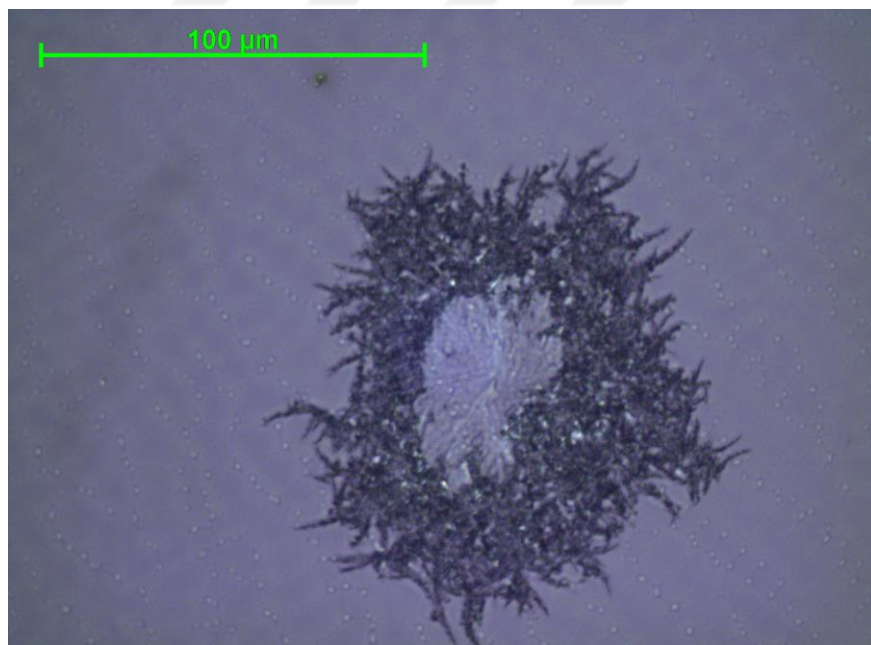


Figure 13. POM image showing the growth of the crystal, A) as-prepared film B) after 3 hours.

Figure 13 shows POM images of an as-prepared film that the solution was intentionally stirred less (10 min) before coating the substrate, to observe the salt crystallization process. The first image (**Figure 13A**) displays an undissolved salt particle in the solution. The image taken after 3 hours shows the crystal growth starting from this undissolved particle. The images emphasize the importance of preparing a clear and homogenous solution before the coating step, to produce a stable film in an LLC phase. As known from crystal growth techniques, defect centers are suitable regions for crystal growth. To be sure that all the ingredients are dissolved homogeneously, the solutions were stirred for 1 day to obtain clear solutions.

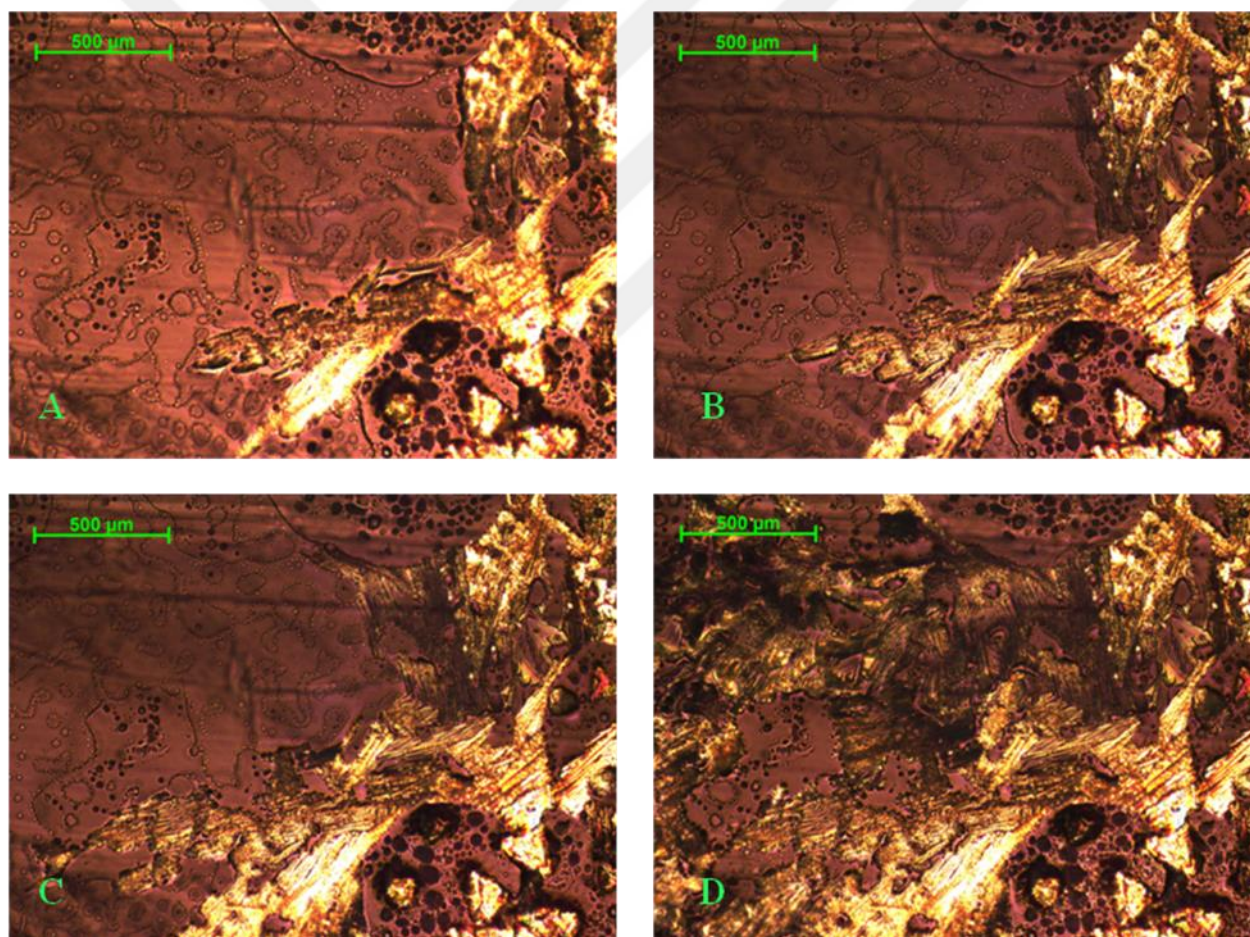


Figure 14. POM images of a sample prepared using drop-casting method, showing how rapid the crystal growth A) 1 hour after the film was coated, B) 2 min later then image A, C) 3 min later, D) 10 min later.

As mentioned before, the LLC mesophase is stable under certain conditions, however when the initial salt crystals are formed, the growth of the crystal is rapid. **Figure 14** shows how rapid the growth of crystallization. When the film was first coated, no crystallization was observed. In the first image (**Figure 14A**) it can be observed that the crystallization was started due to leached out salt after 1 hour. When the film was inspected under POM, although no crystallization was observed up to 1 hour, once bulk crystal was formed, the growth of it is rapid that it grows to cover the entire film in a short time.

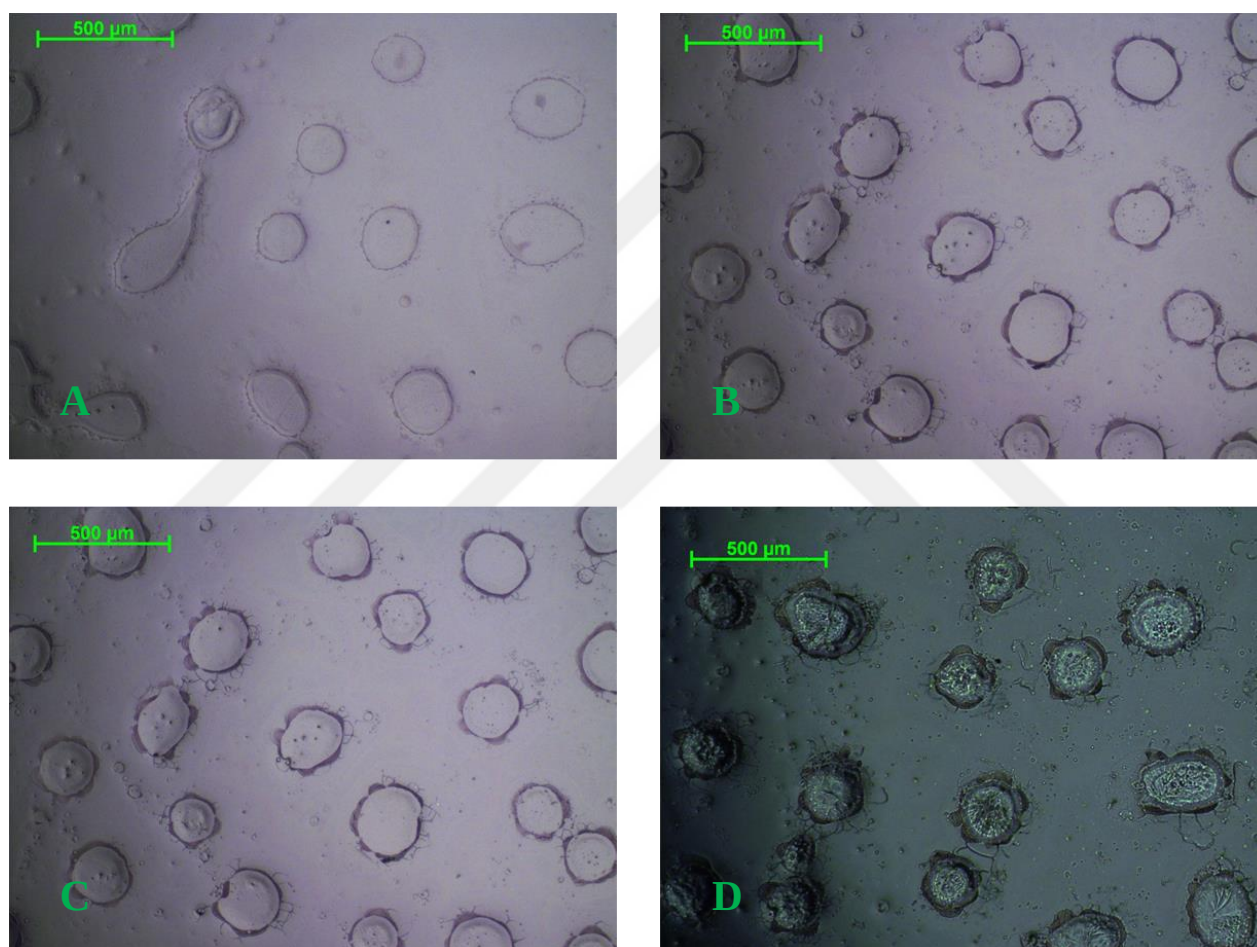


Figure 15. POM images of a sample prepared by dip coating method; A) Fresh sample, B) 3 hours later, C) 9 hours later, and D) 1 day later.

The film in **Figure 14** was prepared by drop-casting method, which produces a less stable film (it will be discussed later). The images in **Figure 15** belong to a fresh film prepared by dip coating method. As shown in the images, there is no crystallization observed even after 1 day. This observation is also consistent with the XRD patterns of the fresh films.

3.1.4 Determination of acid amount

After having an idea of how fresh films behave when salt and CTAB amount is changed, it is important to determine the optimum amount of acid that should be used. In general, the titanium alkoxides condense in water into amorphous titanium oxyhydroxy species upon quick hydrolysis and condensation processes [43] [26]. This rapid polymerization can be hindered by the addition of acid in MASA process. As titania domains polymerize and grow, guest metal ion titania interaction is reduced. By adding acid into the solution, the hydroxide ion concentration is suppressed and the polymerization of titania species can be slowed down. As a consequence, more dispersed titania domains are obtained, which enhances the metal ion-titania interaction for the metal titanate formation. An efficient Ti-O-M bond formation, results in a more ordered mesostructure.

As mentioned before, it is difficult to comment on the lines observed on the small angle XRD patterns. POM images and the appearance of the as prepared films were analyzed to find the role of acid amount on the fresh films. Further measurements were performed after the calcination step by using XRD, SEM, N₂-sorption, and TEM techniques. The POM images display the changes by increasing the acid amount added to the solution. In order to observe the differences more clearly, two samples were prepared, which differed greatly in acid amount. **Figure 16** shows that the image of the fresh sample prepared by using 0.125 g acid displays worm-like features, whereas the sample containing 1 g acid shows a continuous smooth surface morphology.

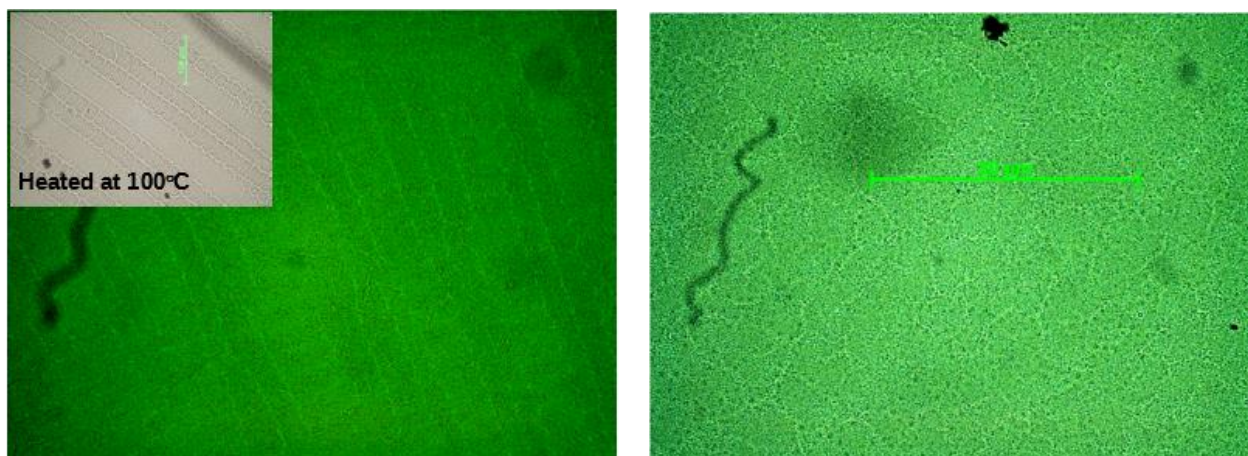


Figure 16. POM image of **(left)** sample containing a low amount of acid (0.125 g), **(right)** sample containing a high amount of acid (1 g).

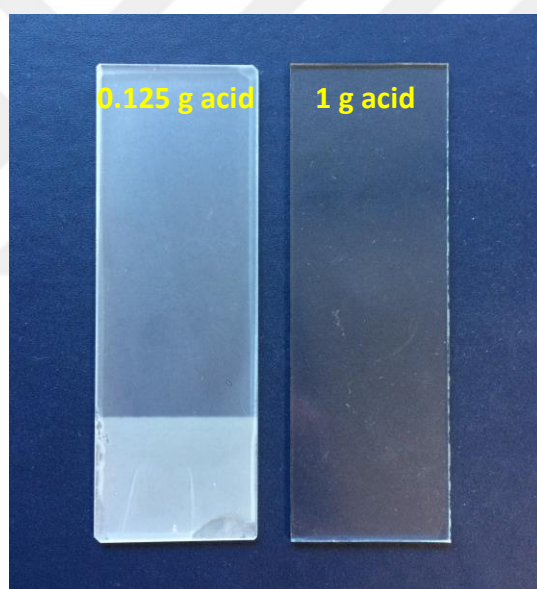


Figure 17. Two as-prepared films with **a)** 0.125 g acid, **b)** 1 g acid after aging for 1 day.

As mentioned before, it is important to obtain an ordered mesophase at the early stages of film preparation to have a good groundwork for later stages. Therefore, obtaining and maintaining a homogenous solution and film before the calcination step is an ideal place to start building a mesoporous structure. **Figure 16** shows that fresh film, prepared with a higher amount of acid, is a more homogenous film and presumably a more ordered mesophase, although it could not be supported by XRD data. Also, **Figure 17** shows that the

film prepared with a higher amount of acid is still transparent and homogenous after aging, whereas the one prepared with lower amount of acid leached out the salt crystals and lost its transparency. This shows that, the mesophase containing a higher amount of acid is more stable over time as the lower one leaches out the salt faster.

3.2 Investigations on Calcined Samples

3.2.1 Typical SEM and TEM images of the calcined films

It is beneficial to introduce the typical SEM images of calcined films to analyze the structures. **Figure 18** displays a general view of a calcined film with bulky crystals at different scales.

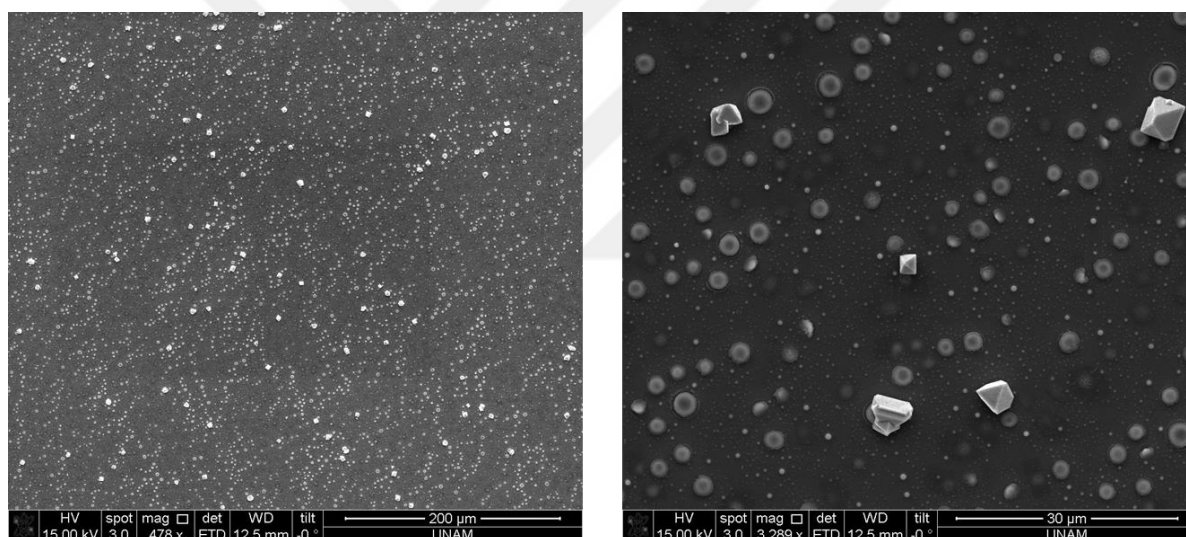


Figure 18. SEM image: an overview of a calcined film.

As shown in the images of the calcined samples, there are 3 different formations on the film; bulk crystals (likely CdO crystals), round small areas, and homogenous porous film material. The following images are going to display these 3 structures in detail.

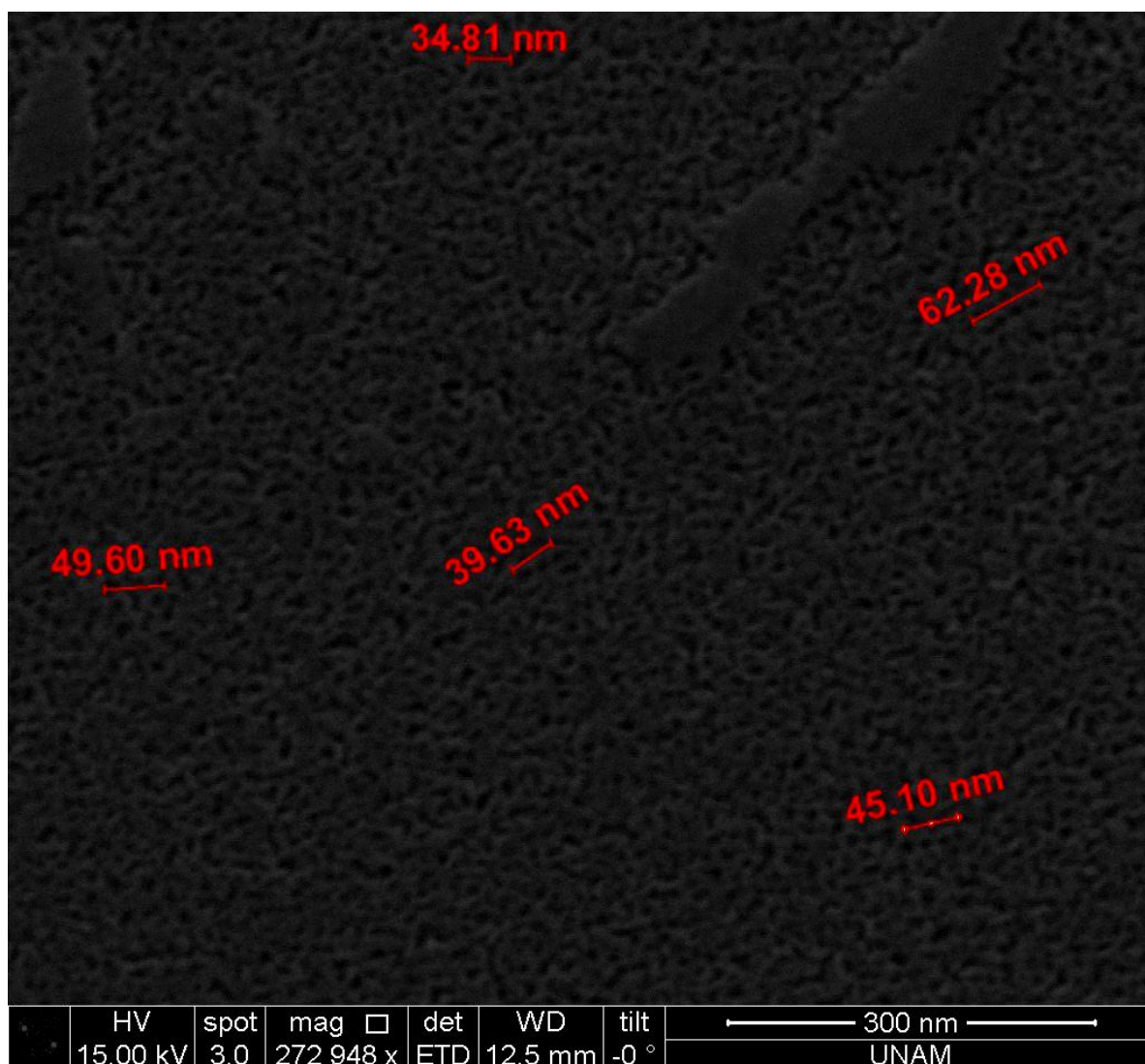
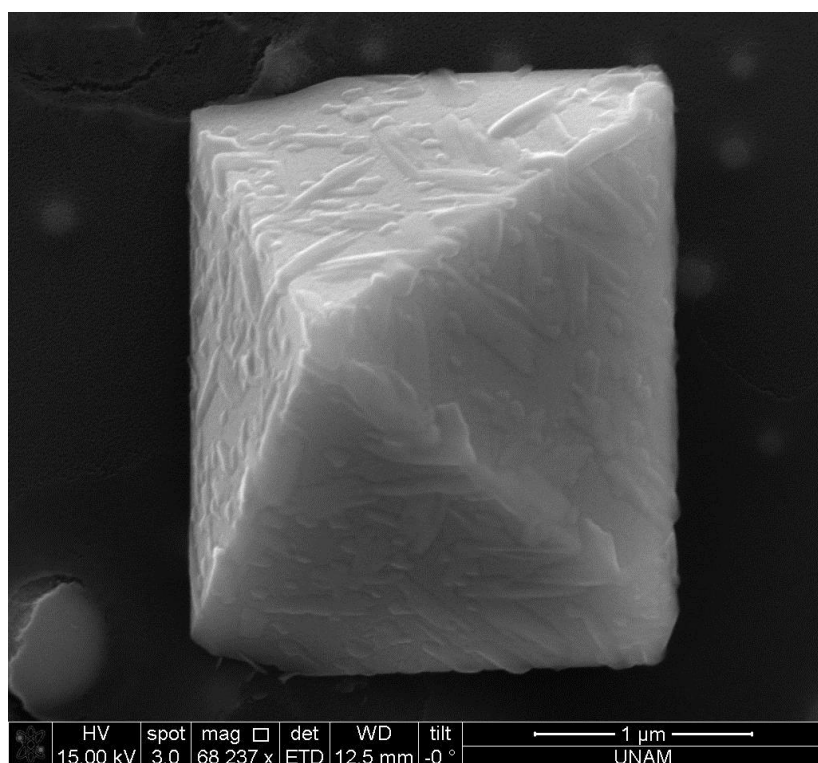


Figure 19. The SEM image of the mesoporous film sample.

Firstly, **Figure 19** shows the film part of the calcined material. The mesoporous film formation can be observed from the images with a pore size of approximately 10 nm. **Figure 20** displays a typical image of a bulk crystal.

A)



B)

D:\SharedData\muammer y\zeynep\270517\270517_003.spc

Label A: Chlorite (Nrm.%= 38.86, 20.96, 34.83, 1.14, 3.84, 0.28)

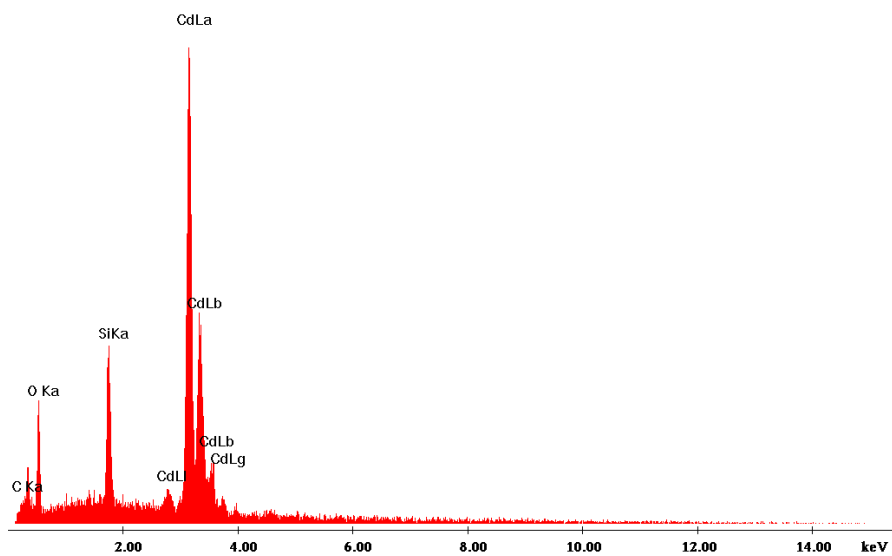
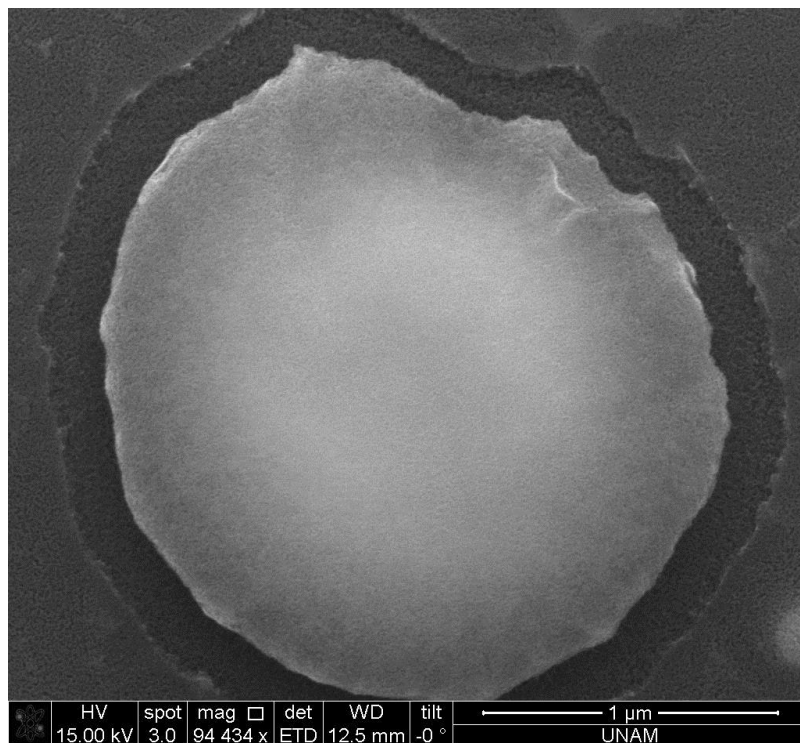


Figure 20. A) A typical image of a bulk crystal on a calcined film and B) EDAX of the displayed area.

As shown in the EDAX spectrum of the crystal, it is cadmium rich, which means these crystals grow out of the leached-out cadmium salt species. **Figure 21** displays the round brighter regions on the film in a smaller scale.

A)



B)

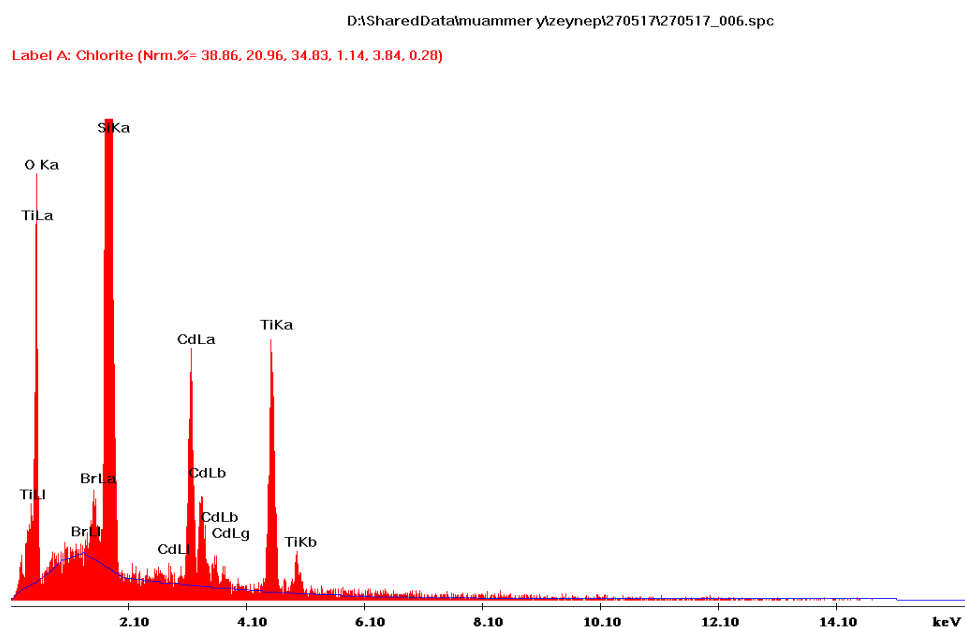


Figure 21. A) A typical image of a round region on a calcined film and B) EDAX of the displayed area.

As shown in the EDAX of the area (**Figure 21B**), the intensities of Ti and Cd are very close to each other, it means that these regions are not that different in terms of components from the desired CdTiO₃ material parts of the sample. These regions (**Figure 21A**) may be forming due to thickening that portion of the sample while the water is evaporating during calcination. Therefore, it can be assumed that these regions are thicker parts of the samples and appear brighter.

Ideally, the entire surface of the calcined sample is expected to be a smooth, homogeneous film without bulk CdO crystals. Changes on the surface composition of the films were observed to sort out the effect of the parameters on the material quality.

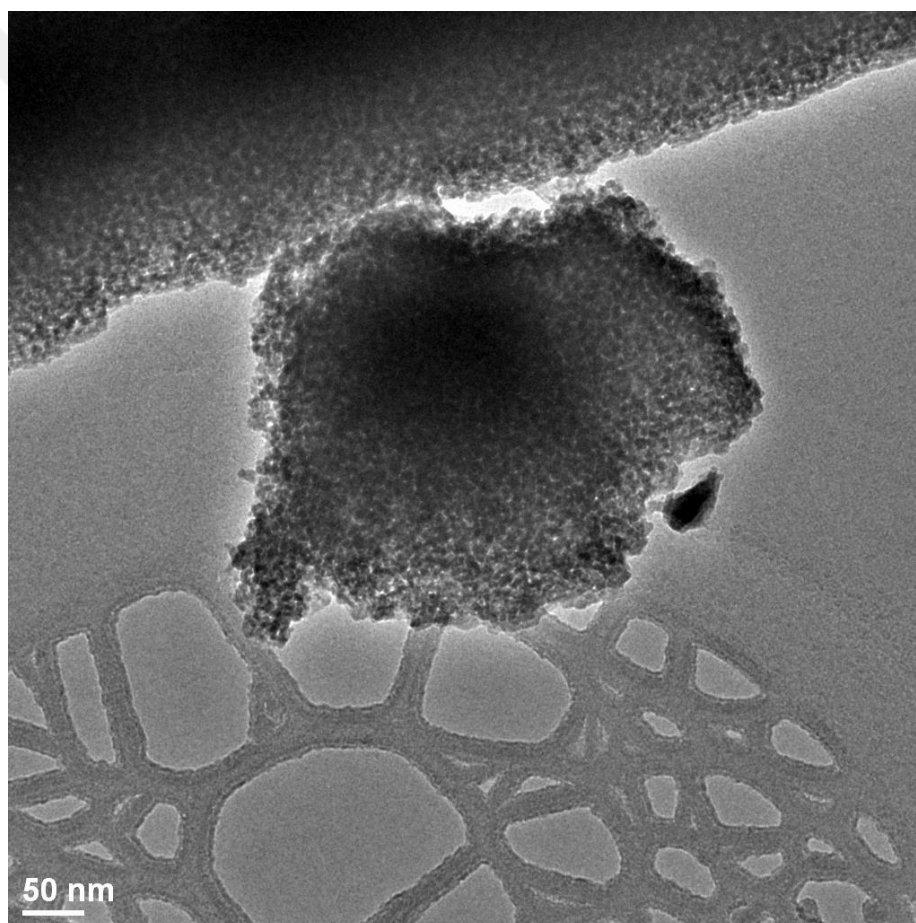


Figure 22. TEM micrograph of CdTiO₃ with a 50 nm scale bar.

The TEM image of the sample (**Figure 22**) also shows that the produced material is a mesoporous film. The image also shows the pores are uniform through-out the film.

3.2.2 Determination of the method

The assembly process starts in the homogenously prepared solution with surfactants and the other substances with a large amount of volatile solvent. The coating method affects the thickness of the films hence the rate of solvent evaporation, which has a critical impact on the interaction of the ingredients to form a well ordered mesostructure.

In this work, dip coating, spin coating, and drop casting methods were used to coat the glass slides before the calcination step. As mentioned before, dip coating method was preferred to coat the films since it gave better results, which will be discussed later.

Dip coating of the homogenous solution on a substrate generally produces monoliths or films [44] [45]. In this process, a glass slide is dipped into a solution and pulled upwards with a constant rate, therefore the evaporation of the solvent starts at the upper parts of the glass slide. A homogenous LC phase starts forming on the surface of the glass slide, as shown in **Figure 23**.

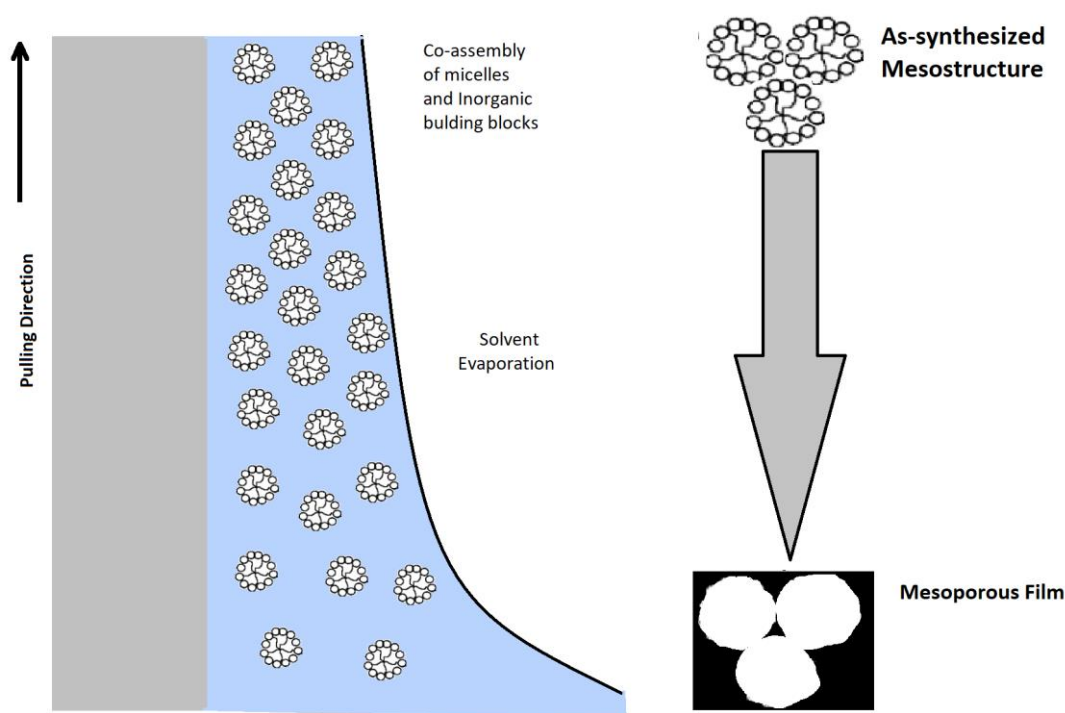


Figure 23. The illustration of assembly of the micelles during coating the glass slides by dip coating method.

The titania species polymerizes and forms a gel-like ordered organic-inorganic mesophase as a film over the surface of the glass substrate. The initial concentrations of the surfactant, titania and metal salt species, besides the dip coating rate, determine the meso-order of the liquid crystalline phase [23].

Figure 24 shows how the films look like after calcination of the fresh films prepared using different coating methods. The orange color shows the presence of CdO crystals over the film. Therefore, observing the colors of the calcined samples gives information about the presence of CdO crystals.

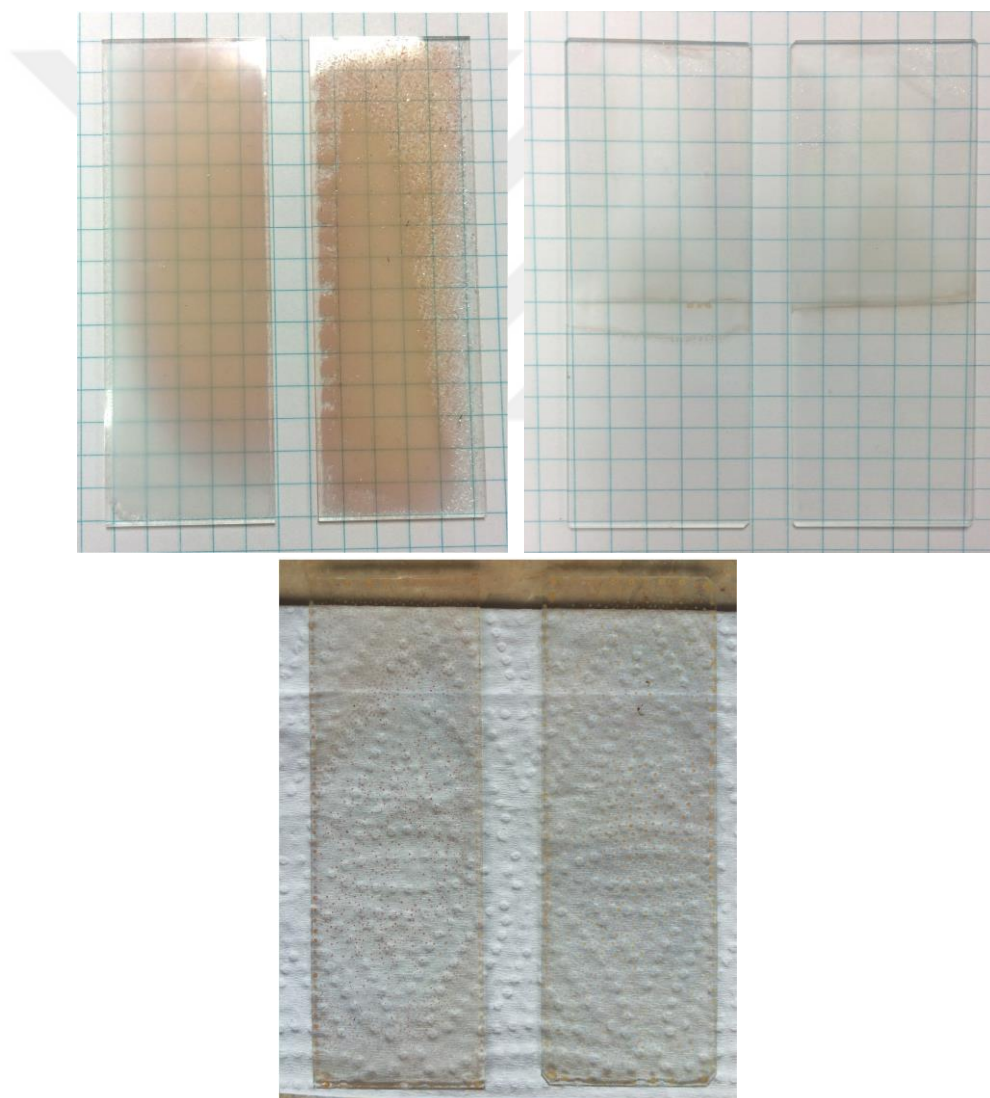


Figure 24. Photographs of the calcined films prepared by a) drop casting, b) spin coating, c) dip coating methods, with the same salt ratios.

The film prepared by drop casting method exhibited an orange color, which indicates the presence of CdO crystals. Preparing the films with spin coating method yielded more transparent and colorless films. However, small orange regions were observed when the film was spanned at 1000 rpm for 20 seconds. Finally, using dip coating method resulted in colorless and transparent films, which may be an indication that there are no CdO crystals or the amount of it is small that it is not even observable.

The XRD patterns of the samples (**Figure 25**) obtained by using three different methods also support the information that obtained from the appearance of the calcined films.

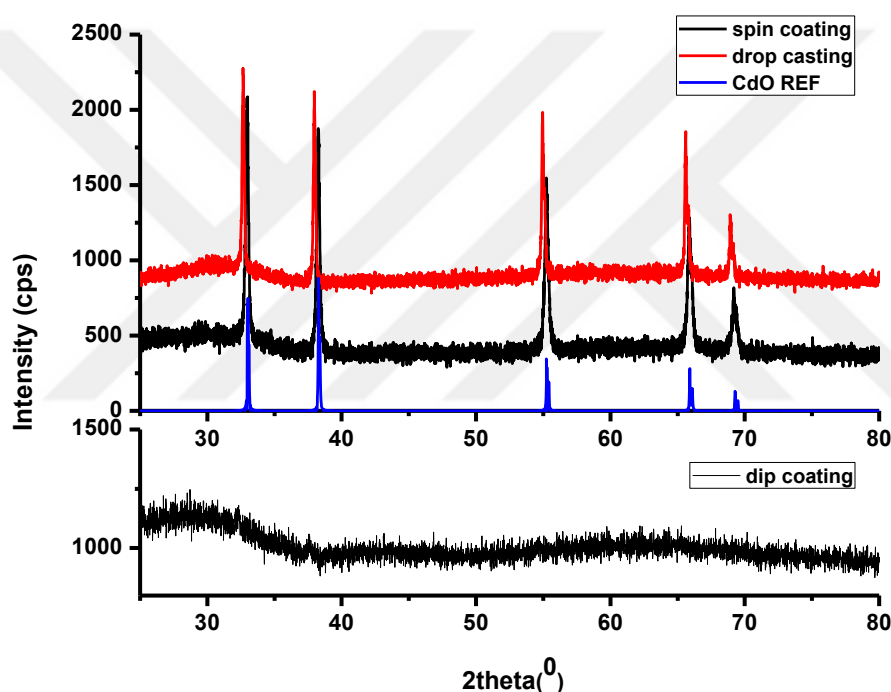


Figure 25. XRD patterns of the samples obtained by drop casting, spin coating and dip coating methods.

The XRD patterns were obtained after calcination of the as-prepared films at a pre-heated oven at 150°C, then it was heated with a 1°C increment to 350°C. The films were heated at 350°C for 30 minutes. The XRD pattern of the sample obtained by dip coating method does not show any diffraction line, the sample is amorphous. However, the samples prepared using the other two methods clearly show characteristic sharp diffraction lines of CdO. The diffraction lines were indexed to CdO using PDF card 00-005-0640.

The SEM images of the calcined samples on silicon wafers also support the results obtained via XRD data, see **Figures 26, 27, and 28**.

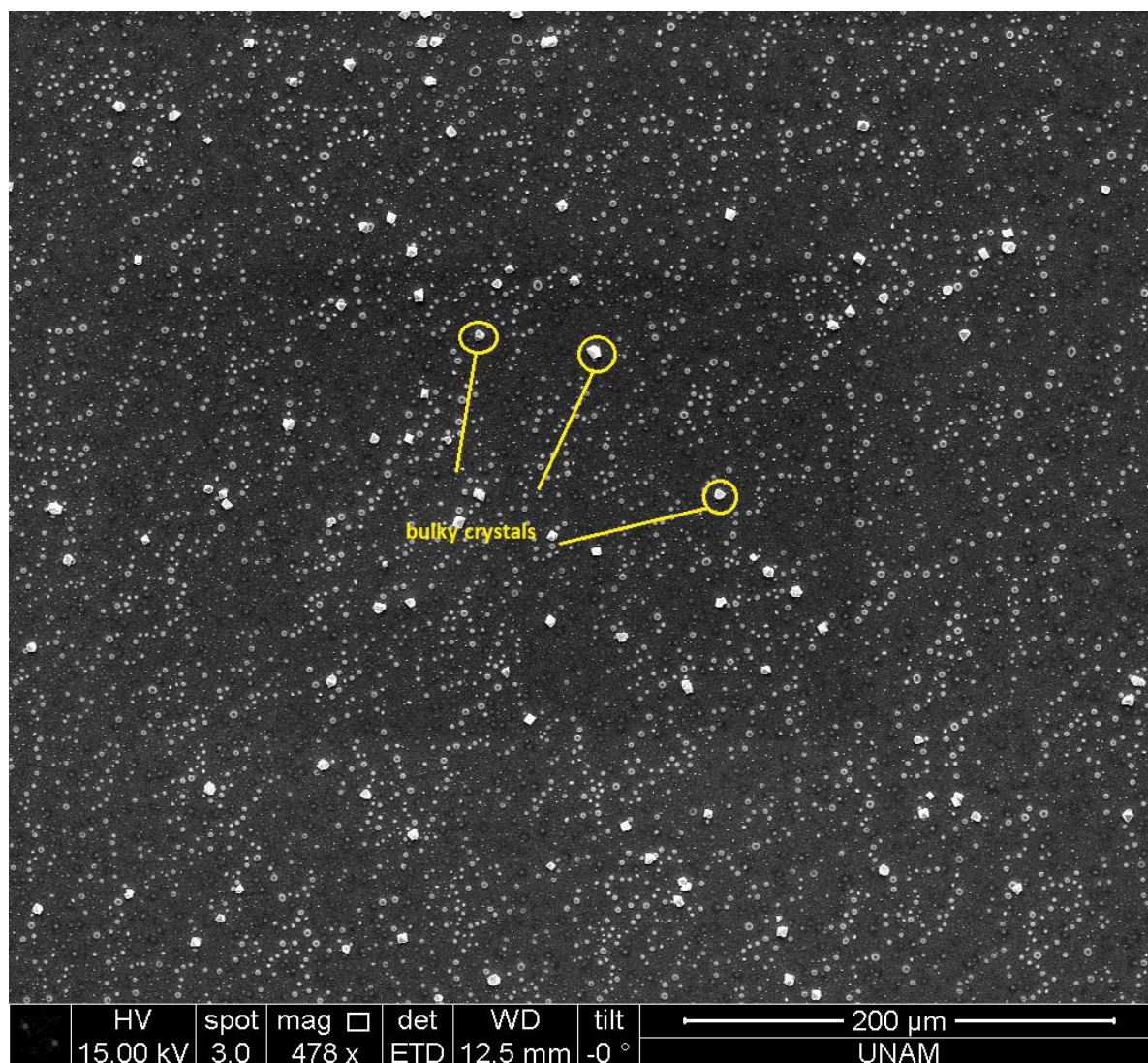


Figure 26. The SEM image of a calcined sample prepared by drop casting method.

Figure 26 displays a typical SEM image of the calcined film, which was prepared by drop casting method. Many bulk CdO crystals (brighter ones) were observed on the surface of the sample together with the bright small round regions mentioned before.

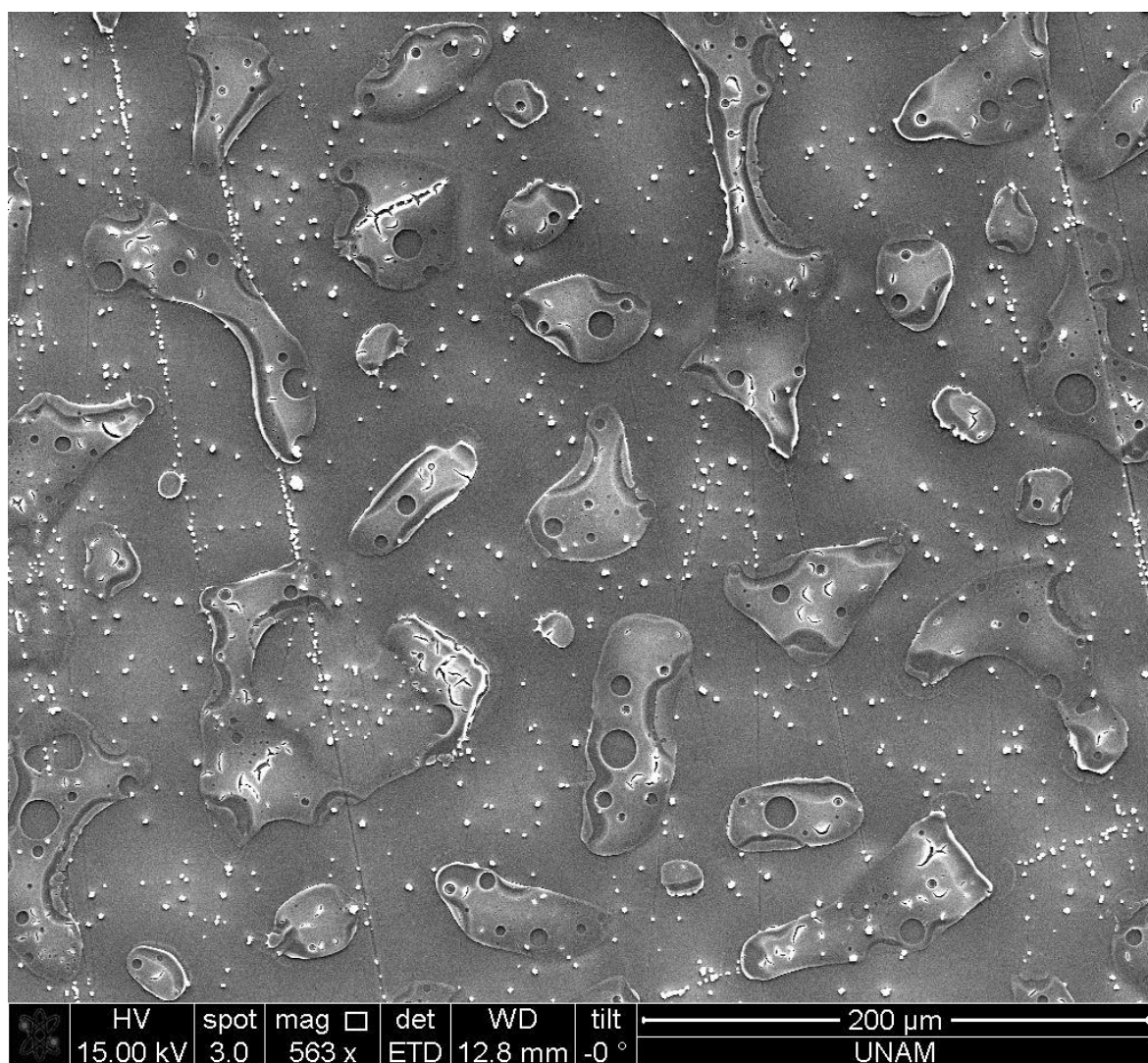


Figure 27. The SEM image of a calcined sample prepared by spin coating method (spanned at 1000 rpm for 20 seconds)

When the coating method was changed to spin coating method, many bulk crystals were still observed while the other bright round regions were not observed. However, the film was still not homogenous and smooth surface as shown in **Figure 27**.

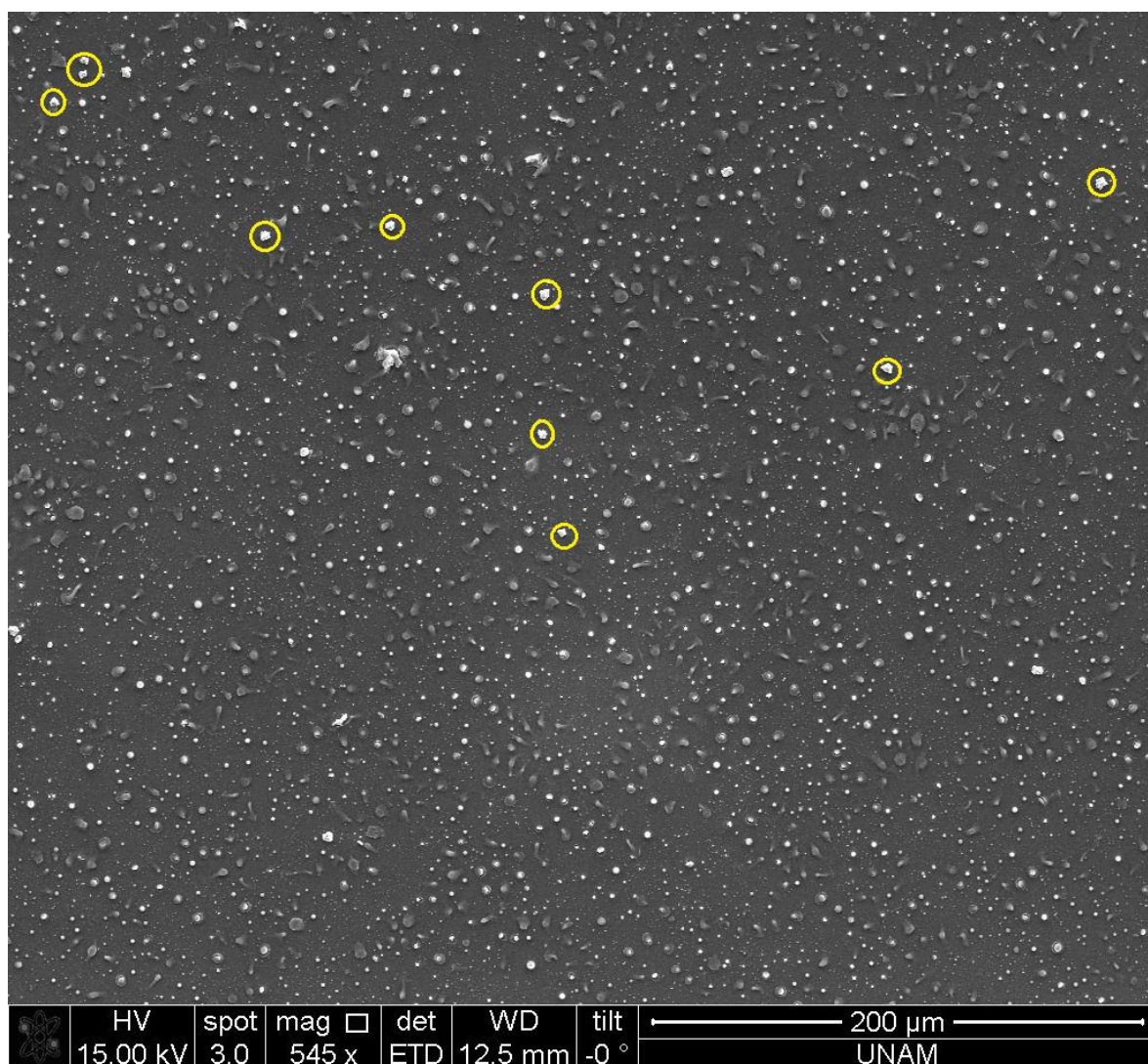


Figure 28 . The SEM image of a calcined sample prepared by dip coating method.

When the preparation method was changed to dip coating method, the amount of bulk CdO crystals (all of them were shown in circles in **Figure 28**) were decreased which is consistent with the XRD patterns of the samples prepared using the same methods. Compared to the other methods the films prepared by dip coating method display a more homogeneous surface with less amount of bulk crystals.

3.2.3 Optimization of calcination process

Investigation of the effects of calcination process on the pore size and structure of the target material will be discussed in this section. The calcination process is a critical process since it is the step, where the actual mesoporous material is formed and metal titanate thin film is synthesized. In this step, the fresh samples upon removal of the volatile species are decomposable and combustible raw materials (surfactant domains, ethanol, and nitrates). Since the synthesis happens in this step, it is critical to optimize the calcination route.

As mentioned before, prior to calcination process, the LLC mesophase is formed by the hydrolyzed titania precursor and the molten salt by guidance of micelles consisting of two different surfactants upon coating on a substrate. However, the LLC mesophase may not be stable for long period since, the surfactants or metal salt may leach out to form bulk salt crystals on the surface of the film. Therefore, it is very important to start the calcination process at the right time and at the right temperature with a proper temperature increment. Upon heating process, ethanol and water evaporates and the carbonaceous species such as CTAB and P123 are burned out and turns into CO or CO₂ gases. Also, oxides of the cations are formed by exchanging the anions with oxygen. Inorganic precursors (titania and metal salt species) react with oxygen to produce the metal titanates. The calcination temperature should be determined delicately to manage all these processes in a right way. It should be high enough to ensure that all the surfactants are burned out. Also, it should not be too high because further heating the material, results in further crystallization and collapse of the mesostructure that will be discussed later.

The starting temperature for the calcination process was determined first. The melting point of the metal salt (Cd(NO₃)₂·4H₂O) is 59.5 °C. Therefore, it is reasonable to start at a temperature above the melting point to ensure that the salt species stay at the liquid phase between the micelles to prevent the salt from leaching out of the LLC phase as bulk salt crystals.

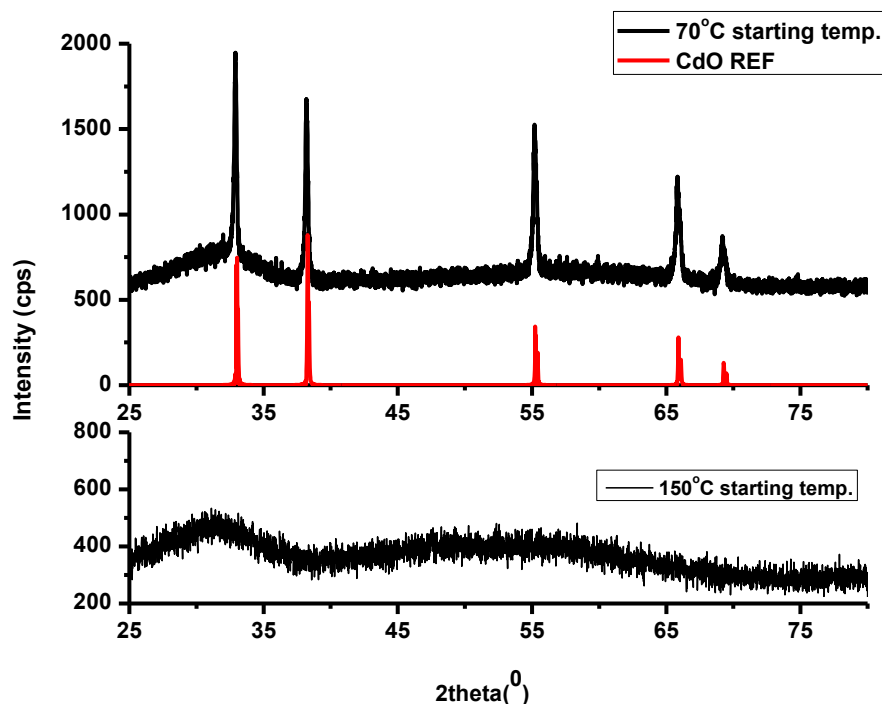


Figure 29. The XRD pattern of mesoporous CdTiO₃ powder, calcined at different starting temperatures.

Two samples were prepared with the same salt ratio (30:1, salt:P123) and same the ingredients but the calcination process of the two samples were started at different temperatures and calcined up to 350°C. **Figure 29** shows the difference between the two samples. When the sample was heated starting from 70°C it was shown that the produced material has a crystalline CdO. When the starting temperature is determined as 150°C, the resulting XRD pattern indicates that there are no CdO crystals in the sample.

In order to observe the crystallinity of the pore walls, a series of XRD patterns were collected. A powder sample was prepared with 50:1 salt:surfactant mole ratio in a solution containing 1 g of acid. The films were calcined by starting calcination temperature of 150°C and annealed up to 250°C. Many films were scraped and the metal titanate powder was collected. After taking the first XRD pattern, the powder was heated up to 350°C, 450 °C, and 550 °C, while recording their XRD patterns in each temperature steps.

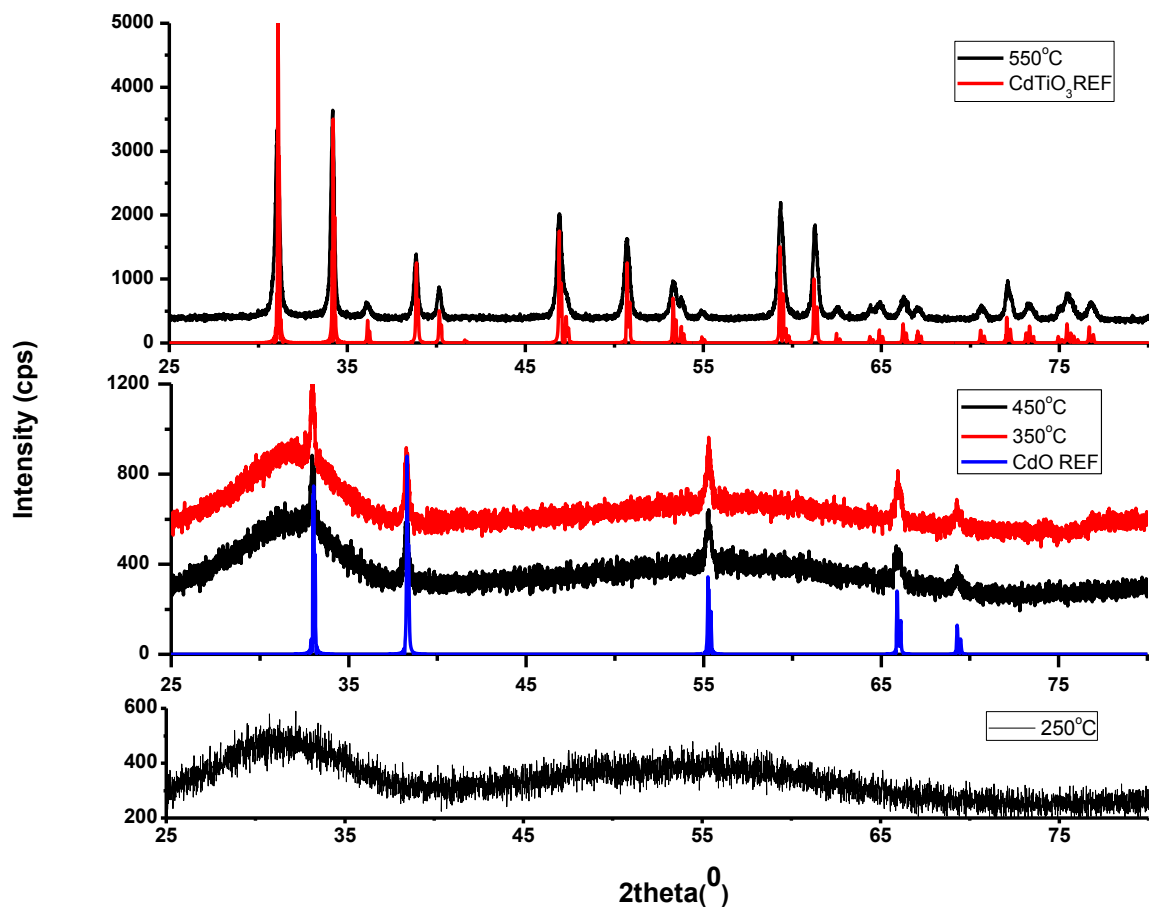


Figure 30 . Temperature (as indicated in the inset) dependent XRD patterns of the mesoporous CdTiO₃.

It is shown in **Figure 30** that, the produced material had an amorphous structure first at 250°C. Upon heating up to 350 °C and 450 °C, the expected crystallization of CdTiO₃ was not observed. When the sample was annealed at 550 °C, a crystallization of the CdTiO₃ phase was noticed. The diffraction lines were indexed to CdO and crystalline CdTiO₃ using PDF cards 00-005-0640 and 00-029-0277, respectively. Consequently, it was concluded that the mesoporous CdTiO₃ is stable up to 450 °C and the structure collapses above this temperature to form bulk CdTiO₃ crystals.

3.2.4 Optimization of metal salt to P123 ratio

All the samples were prepared at a constant amount of Cd:Ti and CTAB:P123 ratios to observe the effect of the changed parameter on the structure like acid or salt amount. It is important to determine the optimum salt amount in the LLC mesophase. As mentioned before, due to soft confinement effect the salt is melted into very small surfactant domains. By increasing the metal salt amount, the liquid phase between the surfactant domains increases. The molten salt does not crystallize even at very low temperatures, which is a critical aspect of MASA [39]. As the molar ratio of Cd:Ti was kept constant to obtain stoichiometric CdTiO_3 , addition of more metal salt to the system means a thicker Cd(II) salt molten to titania layer, results in thicker CdTiO_3 walls. Interaction of the charged hydrophilic domains of assembled two surfactants with metal salt species in the mesophase is the driving force for the LLC formation. Therefore, the addition of ingredients like salt or titania species into the mesophase directly affects the formed mesostructure since the attractive forces that keep the micelles together is affected by the surfactant concentration. The addition of more liquid among the micella domains weakens the attractive forces, which causes the salt to leach out and disrupts the mesostructure at some point. Consequently, it is important to determine the amount of loadable metal ion into the mesophase.

In order to optimize the salt amount, the XRD patterns of the calcined samples which were prepared with drop casting method were observed (**Figure 31**).

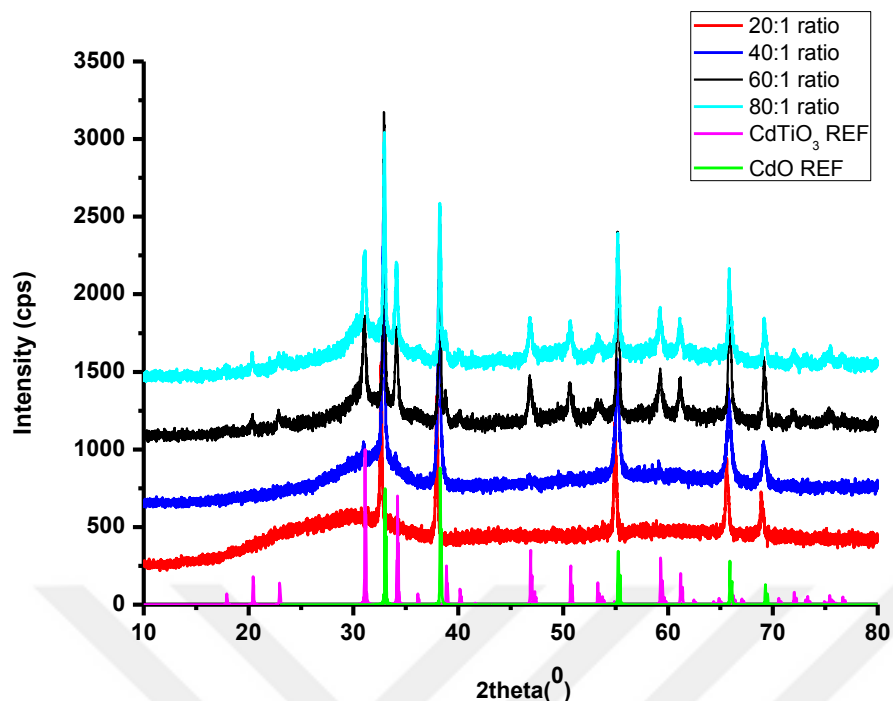


Figure 31 . Salt:P123 mole ratio dependent XRD patterns of the samples prepared with drop casting method.

As shown in **Figure 31**, the samples prepared with drop casting method contain side products in each salt:P123 ratio. At lower salt ratios, the only side product is CdO crystals. As the amount of metal salt was increased, besides CdO crystals, the formation of crystalline CdTiO₃ was observed.

When the method was changed to dip coating method, almost no side products were observed. **Figure 32** shows the XRD patterns of the calcined samples (prepared with dip coating method) with an increasing salt (10:1, 30:1, 60:1, 80:1, 100:1 metal salt:P123 mole ratios) amount.

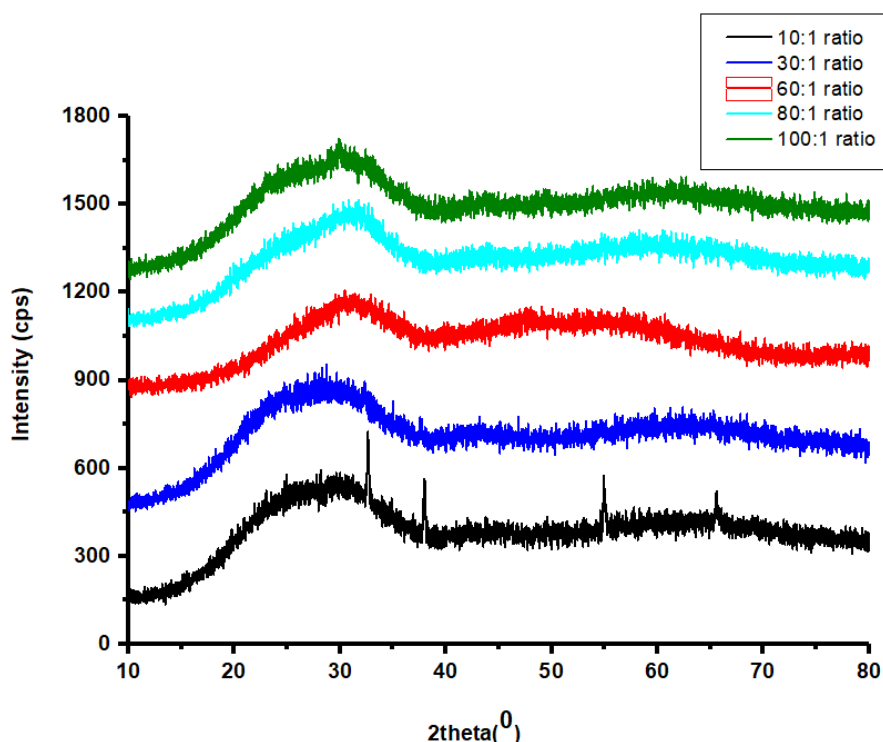


Figure 32 . Salt:P123 mole ratio dependent XRD patterns of the mesoporous CdTiO₃.

The XRD patterns of the calcined samples show that the mesostructure is stable even at very high salt:surfactant mole ratios. There is no crystallization detected by XRD measurements which means the salt does not leach out at high salt concentrations. This is also supported with further analysis (see latter). The diffraction lines at the lowest salt ratio (10:1) belong to CdO crystals as indicated before. The amount of the metal ion needed to form the mesophase and provide the charge balance may not be enough at such low salt ratios.

In the following SEM images, the calcined film samples with different salt:surfactant mole ratios was prepared and they were recorded with the same scales in order to be able to make comparison among them in terms of homogeneity of the films and the amount of CdO crystals. The bulk CdO crystals were marked with yellow circles in order to draw attention to the difference in the number of crystals in that scale and to make them more recognizable. One large scale and one smaller scale images were recorded to show the surface of the films. Both of the images were recorded from a certain area, where they could represent the entire film. Therefore, these images show the general surface features of the samples.

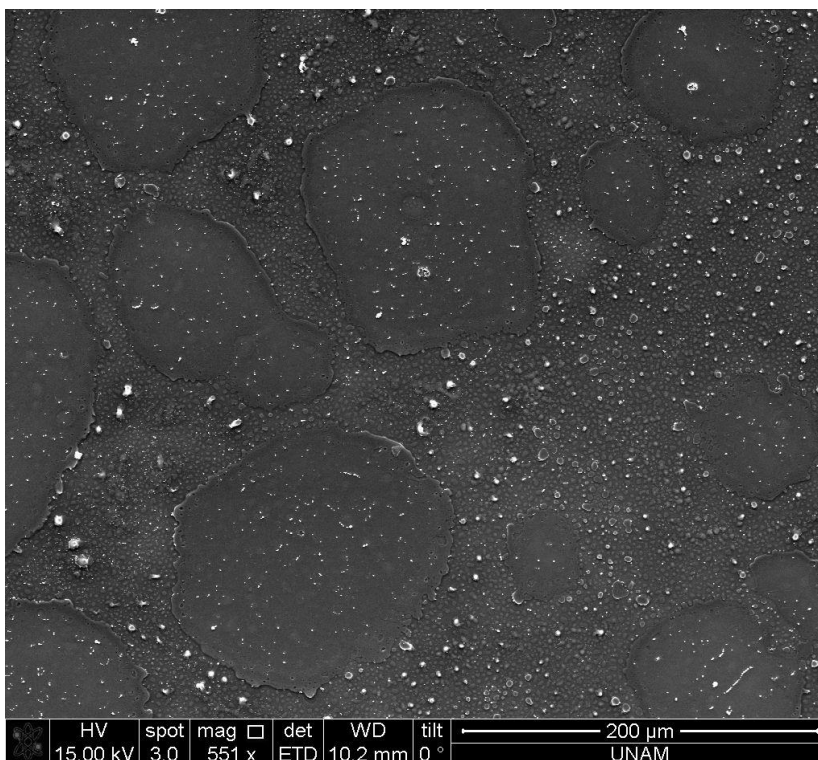
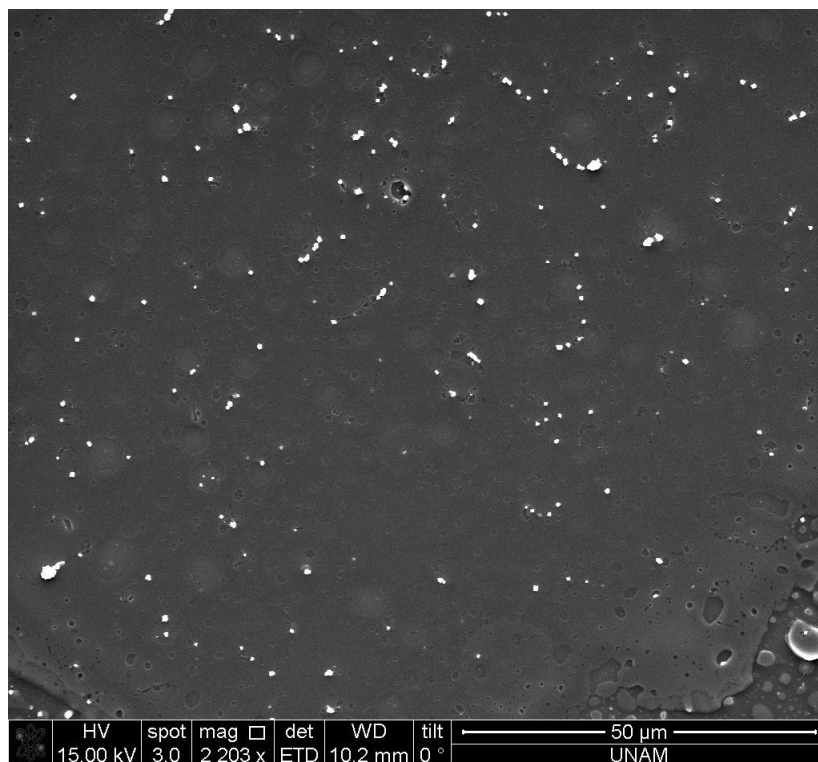


Figure 33 . The SEM image of a sample with 20 salt:surfactant ratio at small (top) and large (bottom) scale.

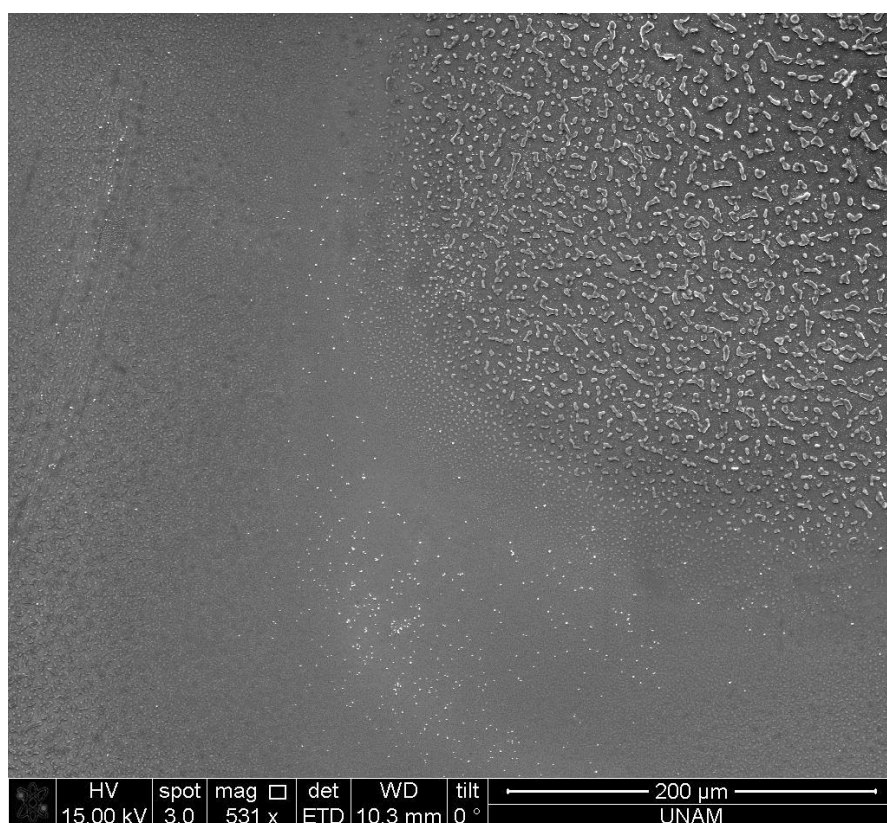
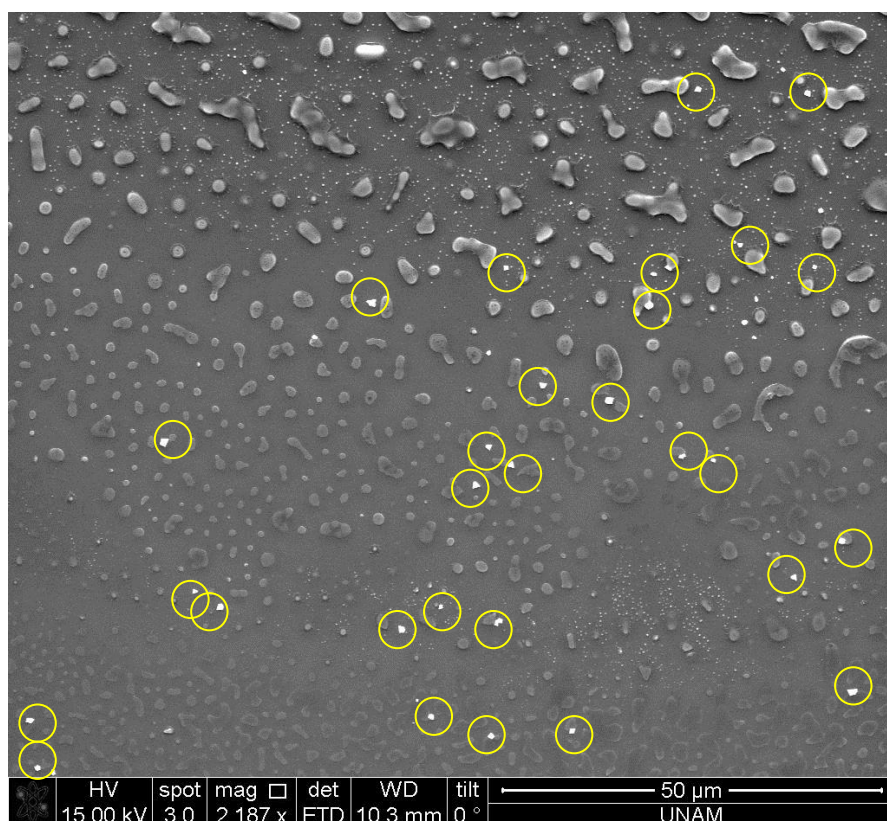


Figure 34 . The SEM image of a sample with 40 salt:surfactant ratio at small (top) and large (bottom) scale.

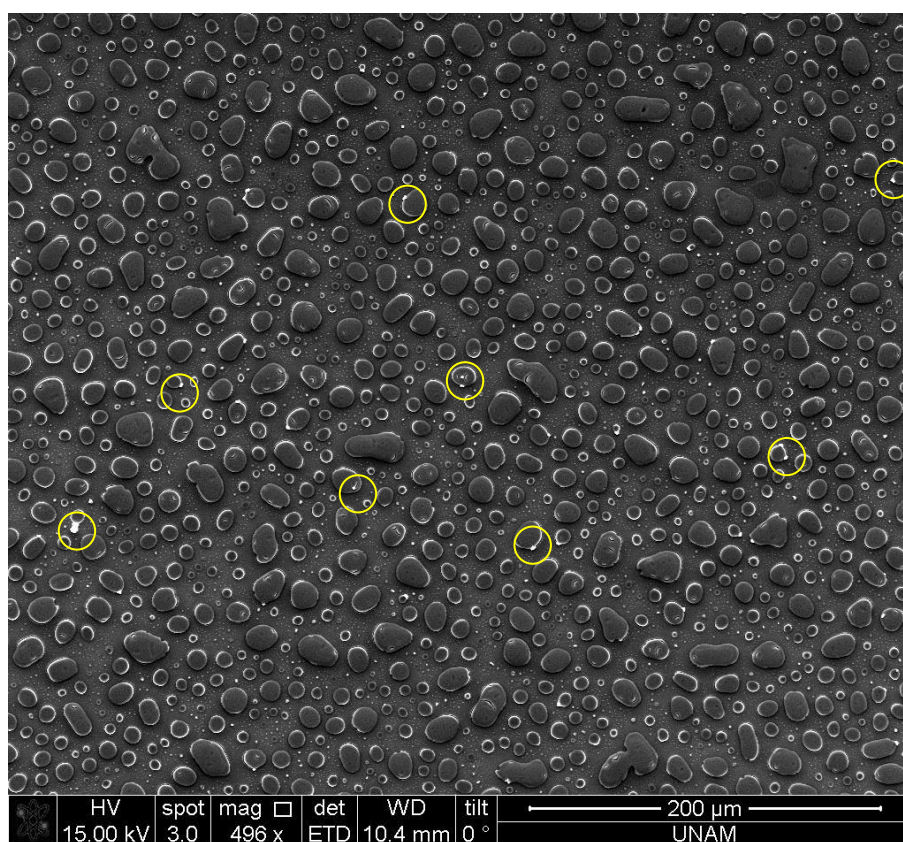
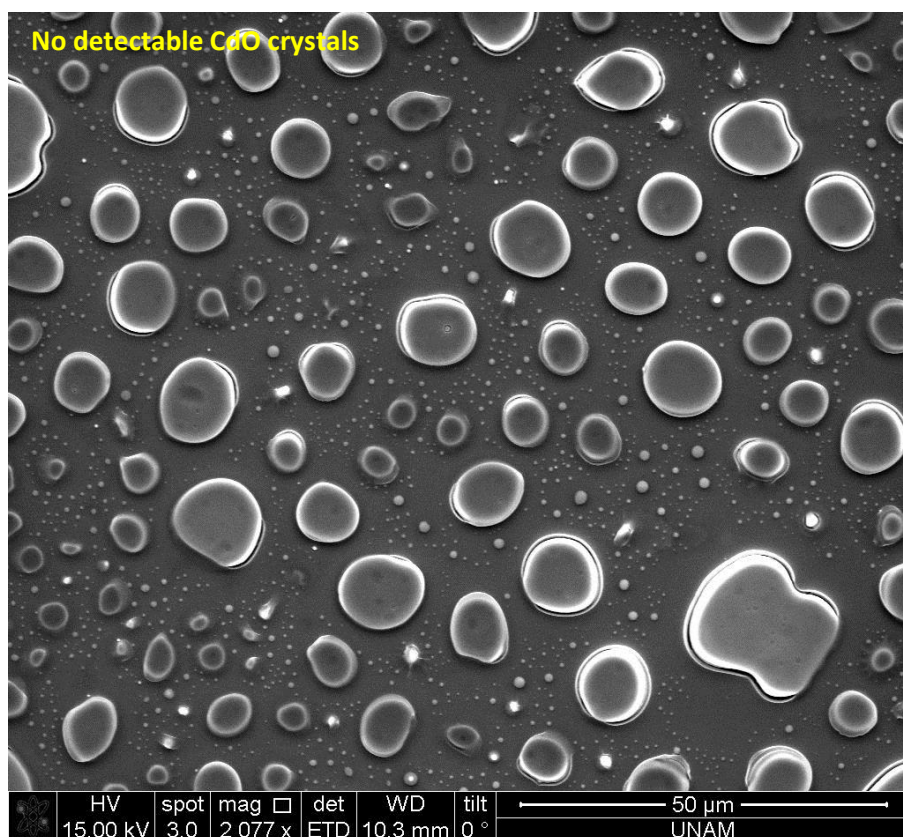


Figure 35 . The SEM image of a sample with 60 salt:P123 ratio at small (top) and large (bottom) scale.

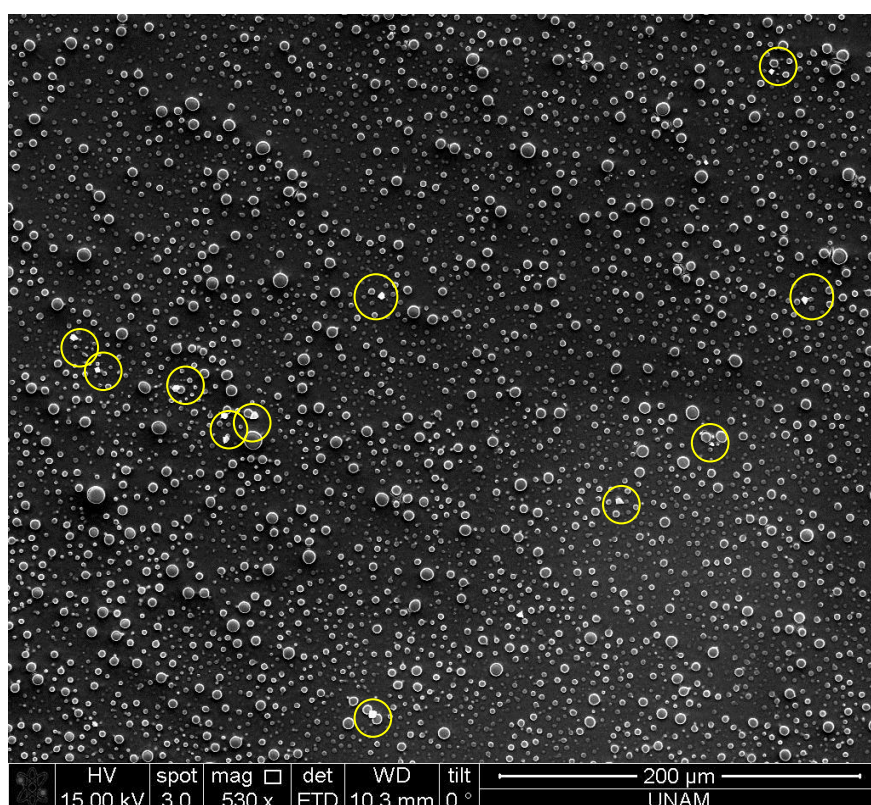
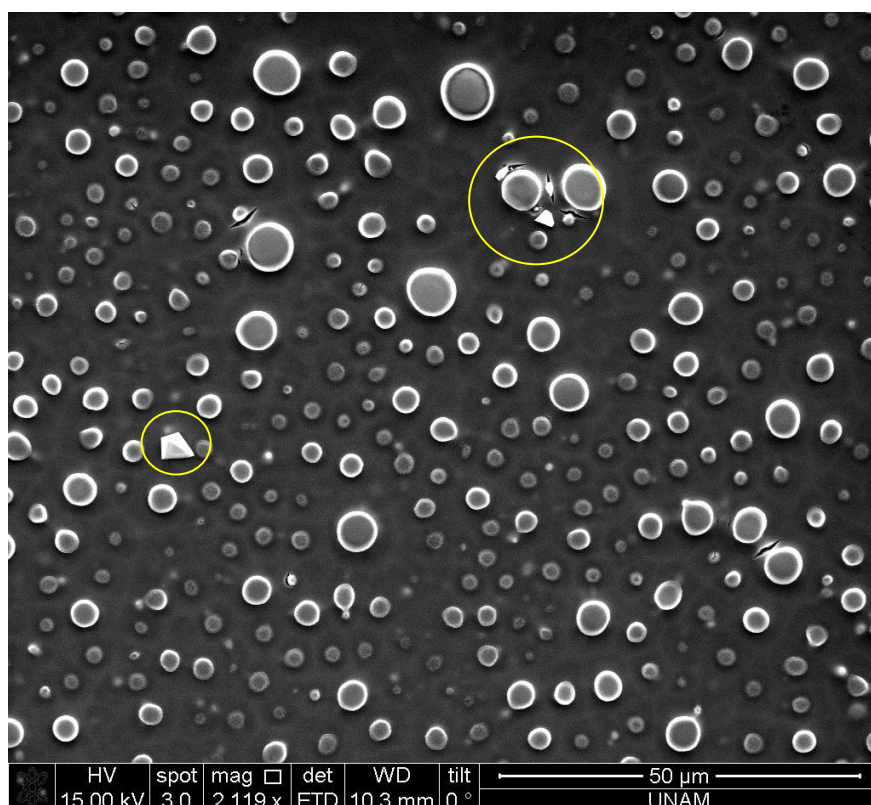


Figure 36 . The SEM image of a sample with 80 salt:P123 ratio at small (top) and large (bottom) scale.

The images of the calcined films were taken to have a general idea about the change when the salt ratio of the sample was increased before further analysis. Firstly, it should be noted that the crystals in the images were not detectable by the XRD and therefore it can be said that the CdO crystals, observed in the images, are not present in the calcined film samples in large quantities. Since the amount of the crystals was too much, in **Figure 33** the CdO crystals were not circled in order not to hinder the overall view of the image. Although it is not the case in the other images, in the small scale image of **Figure 33**, nearly all the bright structures were CdO crystals. As mentioned before, the magnified images are chosen in a way that it can represent the structure of rest of the film, especially in terms of the amount of CdO crystals. The larger scale images were also introduced in order to show that the magnified images are representative of entire film. When the salt ratio was increased to 40, it was observed that the film got more homogeneous and the number of CdO crystals was decreased. All the crystals were circled in the magnified image in **Figure 34**. When the large scale image was examined, it was observed that the crystals were concentrated in certain regions of the film but they did not exist in the majority of the sample. In **Figure 21** it was shown that the round-bright regions were a part of the film that has similar structures in terms of components with the material desired to be synthesized. When the image in **Figure 35** is compared with the previous ones, it can be seen that there are less crystals showing up in the images both in small and large-scale images. The bright parts of the magnified image in the **Figure 35** are not CdO crystals, they are the same bright-round regions as the image in **Figure 21**. These regions are likely thicker part of the samples and charged more to appear bright. When the large-scale images of **Figure 34** and **35** are compared, it is seen that although the sample prepared with 60 salt ratio seems to have less amount of crystals, it has a more uneven surface which is not desired. Therefore, in the proceeding experiments, our investigations were mainly concentrated on the samples containing 50 salt:surfactant mole ratio. It was shown that the sample containing 20 salt ratio had more crystallization compared to the samples with higher salt ratios. Since there is a charged surfactant in the media, addition of the metal ion provides a charge balance between the surfactant domains and the liquid between them, which enables self-assembly of the ingredients and holds the LLC mesophase stable. Since the amount of the metal ion that is needed to form the mesophase and provide the charge balance is not enough, the formation of the mesostructure may be more difficult or the stability of the formed mesophase would not be long enough to synthesize the desired material.

Figure 36 displays the image of the sample prepared using 80 salt:P123 mole ratio. Compared to 60 mole ratio, surface of the sample was still uneven but more crystals were observed. After calcination of the samples, surfactant domains are burned but the liquid between the surfactant domain containing the metal salt and titania precursor stays to form the desired material. As the amount of liquid is increased by adding more salt and titania to the media to increase the salt:surfactant ratio, thickness of the film is also increased. The remarkable point in this image is that the formed film begins to crack due to its thickness. As mentioned before, cracked regions are more suitable regions for crystal growth. The CdO crystals growing out from the cracks can be seen from the magnified image in **Figure 37**.

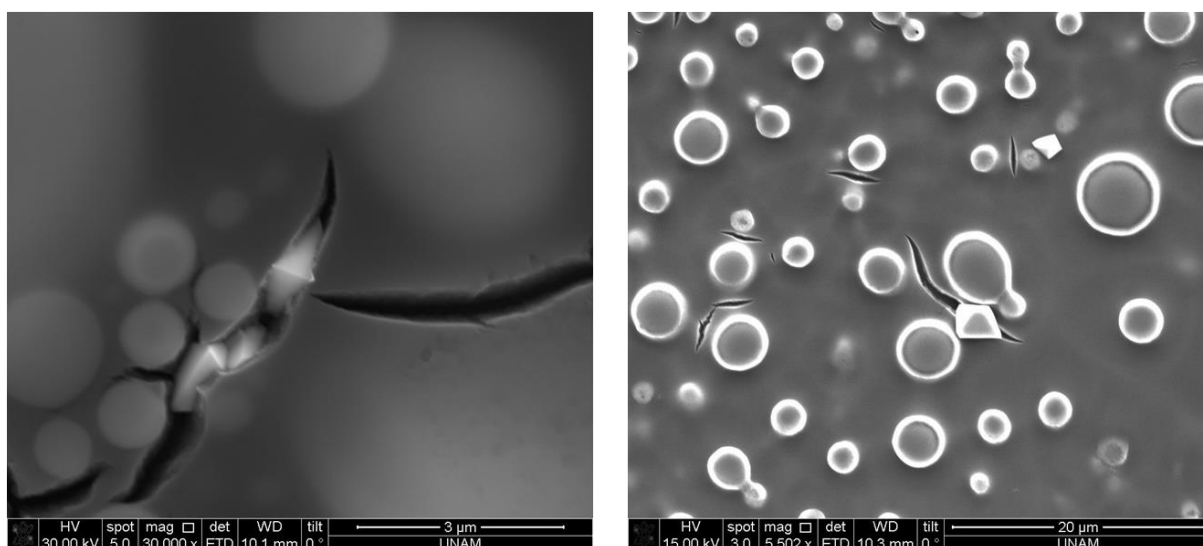


Figure 37. SEM images, showing crystal growth from cracks.

Although producing thick films is useful to obtain more material in a shorter time, the fact that the cracks can cause salt leaching is a disadvantage.

The information obtained from the SEM images is consistent with N₂-sorption measurements of the calcined samples. Three different samples with 20, 50, and 80 salt:surfactant mole ratios were prepared by scraping many films to collect the adequate amount of powder for N₂-sorption measurements. To prepare the samples, the acid amount of the solution was also increased to keep the concentration constant as 0.4 g, 1 g, and 1,6 g acid. To determine the surface area, Brunauer-Emmett-Teller (BET) surface area calculations were used. Moreover,

in order to determine the average pore size and plot the pore size distribution Barrett-Joyner-Halenda (BJH) calculations were used.

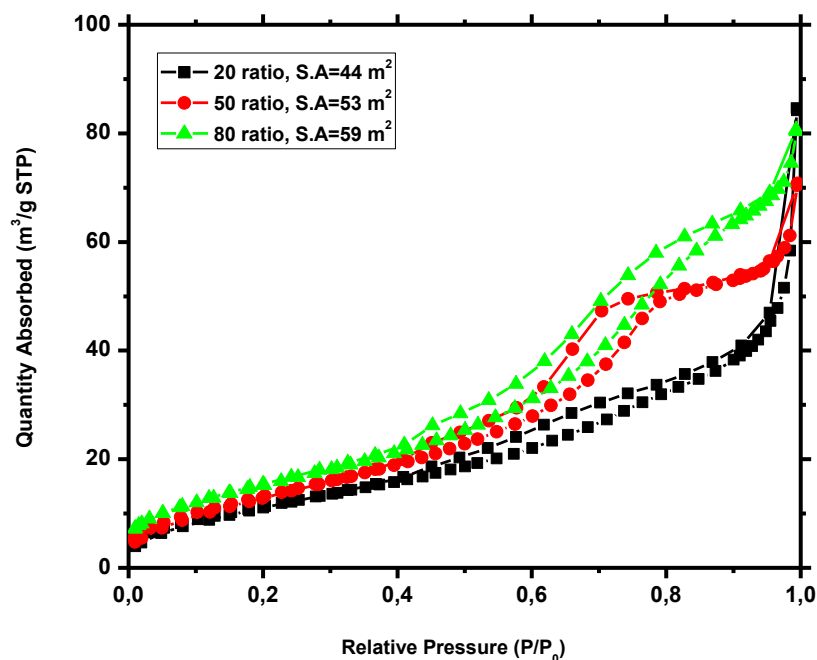


Figure 38. N₂ sorption isotherms of the samples with an increasing salt:P123 mole ratio calcined at 350°C

The isotherms of the samples are type IV with hysteresis, which is characteristic for the mesoporous materials. As estimated from the SEM images, the smallest BET surface area belongs to the sample with 20:1 salt:P123 mole ratio as lots of bulky CdO crystals were observed on top of the film. Note that bulk structures result in a decrease in surface area of the sample. The nonporous bulk structures, like CdO crystals, contribute to the total mass, without contributing the surface area. Therefore, decreases in surface area of the samples can be attributed to formation of more bulk crystals.

The BET surface areas of the 50 and 80 salt ratios are 53 and 59 m²/g, respectively and are relatively close to each other.

Samples	BET surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
20 salt ratio	44	3.4	0.13
50 salt ratio	53	5.9	0.11
80 salt ratio	59	3.5	0.13

Table 2. Salt ratio dependent N₂ sorption data of mesoporous CdTiO₃.

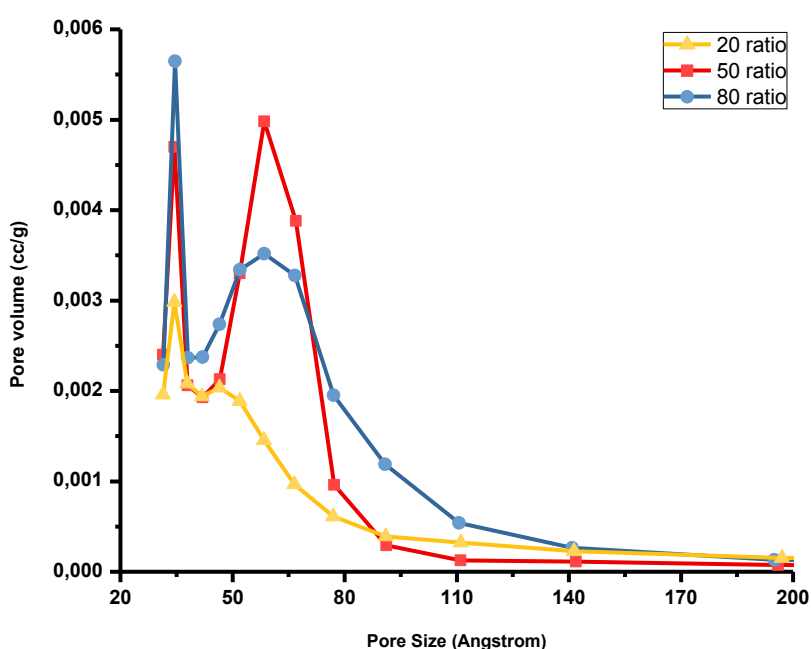


Figure 39. Pore size distribution of the samples with different salt amounts.

It was clearly shown that the 20 salt ratio should not be the choice for further investigations. Since there was not much of a difference between 50 and 80 salt ratio, 50 salt ratio was chosen to avoid excessive salt and too much thickness that may both result in the salt to leach out. The XRD measurements and the SEM images of the calcined samples at lower salt compositions showed the presence of remarkable amount of CdO crystals and consistent with N₂ sorption results. The pore size distribution plots clearly show that the materials in all

compositions are similar and display a smaller pore-size, around 2 nm and a large one around 3.4 nm. As shown in the **Figure 39**, there are 2 different pore systems in terms of their sizes. The smaller ones are formed after the surfactant domains are burned during the calcination. As the reaction goes, these pores start to unite with each other and form larger pores. The average pore sizes are 3.3 (smaller pores) and 4.6 nm (larger pores) for 20 ratio; 3.4 and 5.9 nm for 50 ratio; and 3.4 and 5.8 nm for 80 ratio.

3.2.5 Optimization of amount of concentrated nitric acid

Rapid polymerization of titania speices are hindered by addition of acid in MASA process. Since the polymerization of titania species hinderes the active sides for metal-titania interaction, it is important to slow down the polymerization of titania species. Adding concentrated nitric acid to the solution suppresses the hydroxide population, which enhances an efficient Ti-O-M bond formation and favors a more ordered mesostructure.

The following SEM images show the change of the surface features of the calcined films when the acid amount is increased.

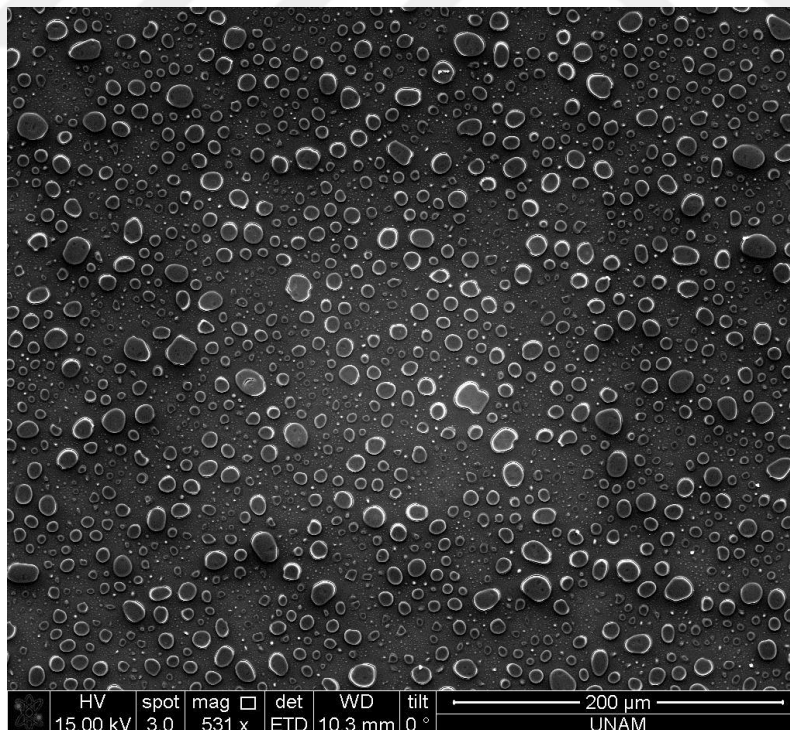


Figure 40. Image of the sample with 50 salt:P123 ratio, containing 1 g acid.

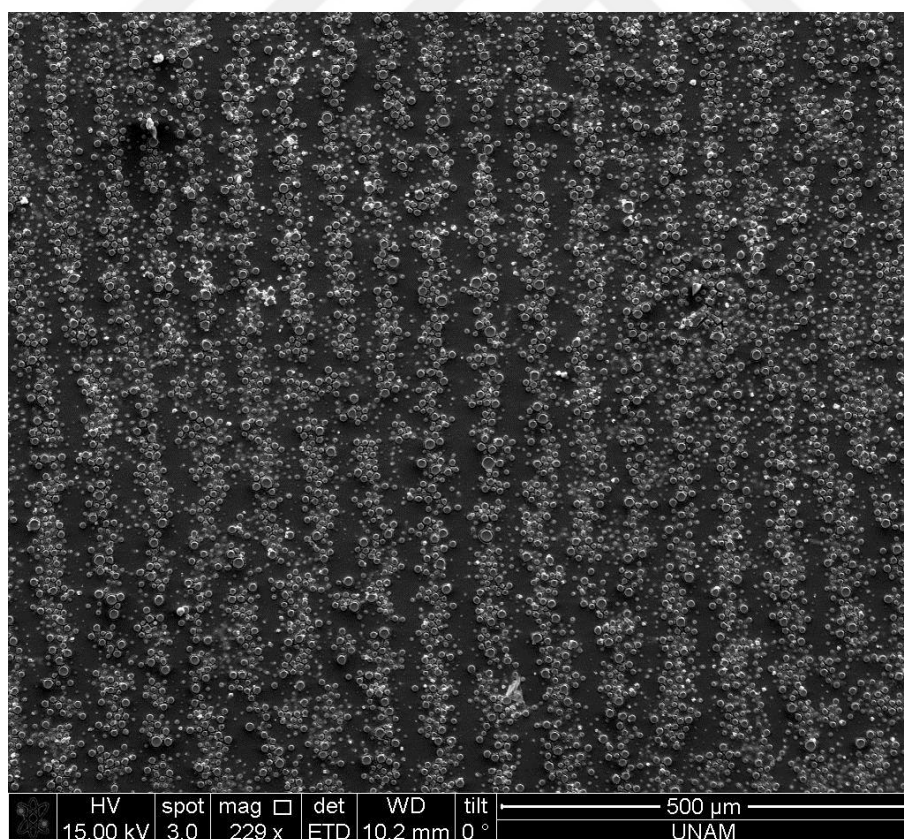
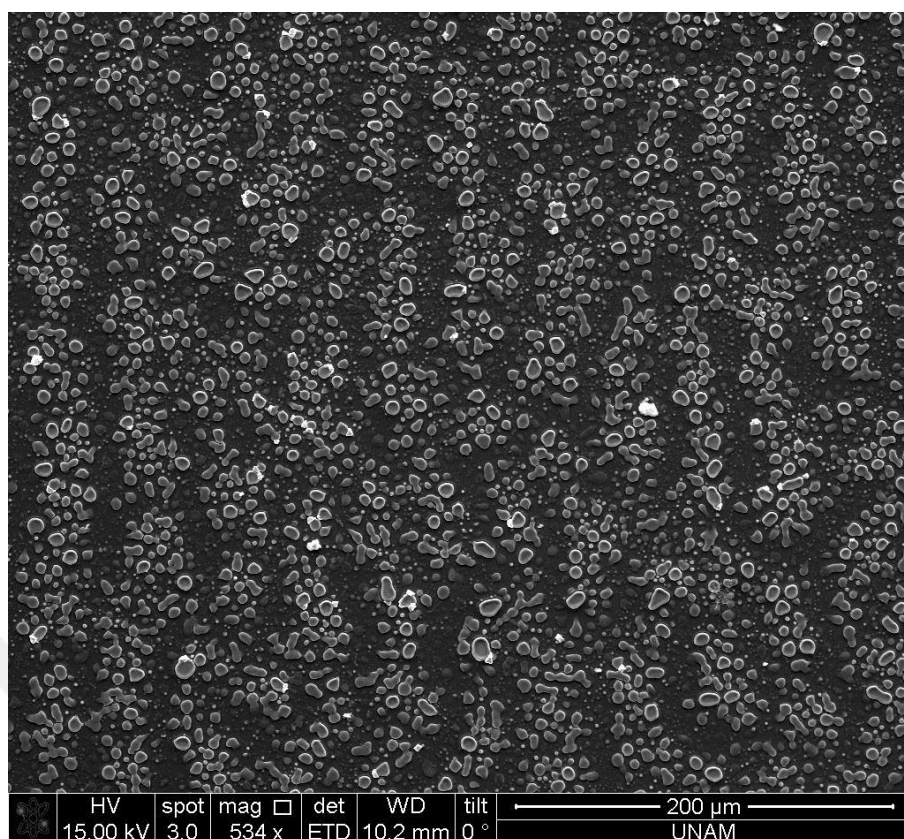


Figure 41. SEM images of the sample with 50 salt:P123 ratio, containing 3 g acid.

While studying on the fresh samples, it was observed that putting low amount of acid (0.125 g) causes the salt to leach out faster and putting higher amount of acid (1 g) results in a more continuous smooth surface morphology. After observing that, for calcined films samples, the comparisons were generally made with respect to the amount of 1 g of acid. The samples shown in **Figures 40 and 41** were prepared using 50 salt:P123 salt:surfactant mole ratio and calcined at 350°C. While preparing the solution 1 g and 3 g of acid were put into the solution, respectively. The amount of 3 g was chosen intentionally to see the effect more clearly. As seen from the images, the sample containing 3 g of acid had a more uneven surface morphology compared to the one with 1 g acid. The amount of undesired bright-round structure was increased. Since a film having a smooth and even surface is desired to be produced, these images gave the idea that increasing the acid hence the water amount up to 3 grams may not be useful. As adding a low amount of acid (0.125 g) does not seem to work well in this system, adding a high amount of acid may bring other disadvantages. Although the quick polymerization of titania species in water is suppressed by addition of the acid up to a certain point, it should be noted that concentrated nitric acid contains 32 % water. By adding the concentrated HNO_3 a considerable amount of water is also added to the media as well. While adding a low amount of acid to the system, the amount of water added with it may not be dominant; however, it becomes significant at very high amounts of acid and may affect the condensation and hydrolysis reactions of the titania species. This situation hinders the metal salt and titania interaction which subsequently leads the formation of other oxides like CdO of TiO_2 . Eventhough it is difficult to comment on the formation of bulk CdO crystals by SEM images, it is clearly seen that adding excessive amount of water results in a more uneven surface morphology.

The effect of change in acid amount was also investigated by N_2 -sorption measurements.

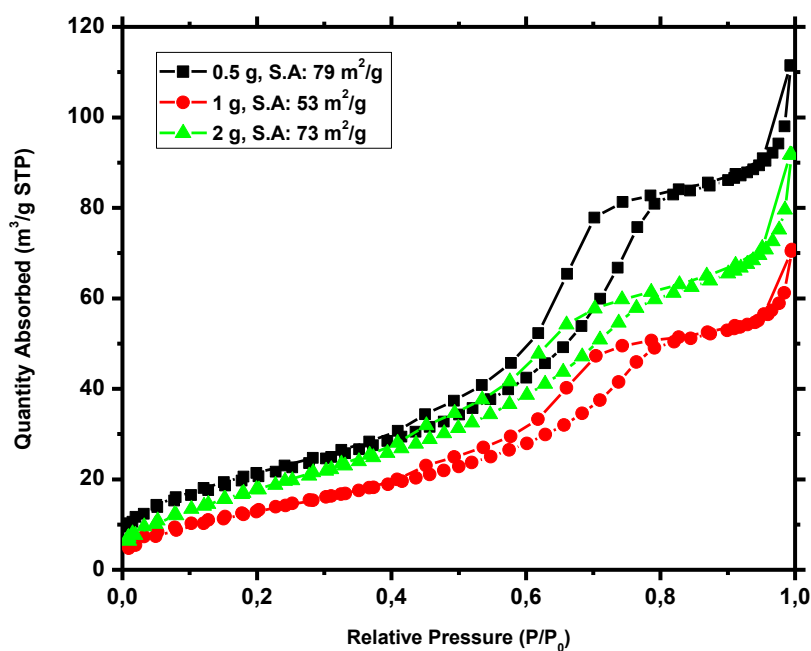


Figure 42. N₂-sorption isotherms of the samples prepared at the same salt ratio but changing acid amounts as 0.5 g, 1 g, and 2 g.

As shown in the isotherms in **Figure 42**, there is not an ordered increase in surface area of the samples with increasing acid amount. 0.5 g acid gave the highest surface area.

50:1, salt:P123 mole ratio	BET surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
0.5 g	78	5.9	0.18
1 g	53	5.9	0.11
2 g	73	3.5	0.14

Table 3. Acid amount dependent N₂-sorption data of mesoporous CdTiO₃.

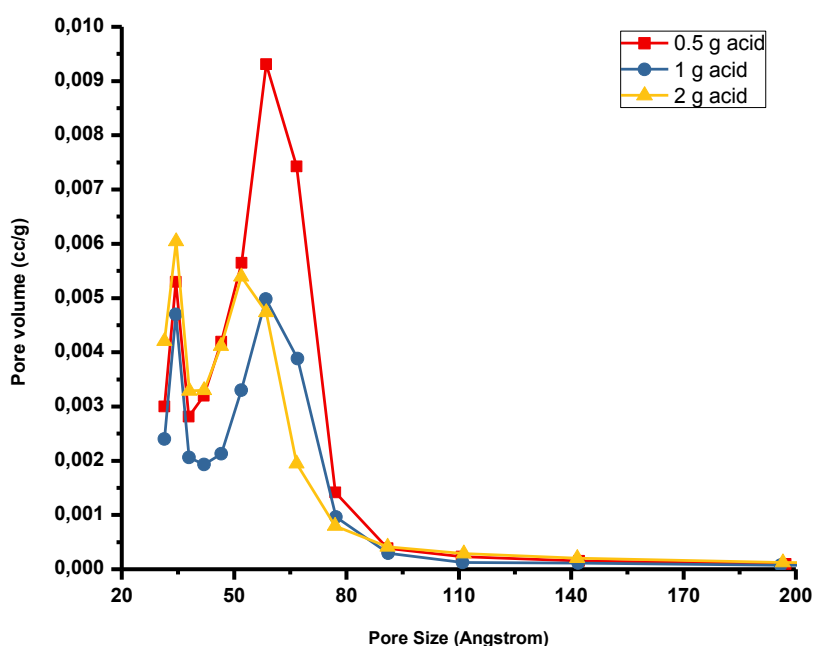


Figure 43. Pore size distribution of the same samples in Figure 39 using different acid amounts.

The sample prepared with 0.5 g acid showed a higher surface area and a more uniform pore size distribution. Although it is difficult to comment on a regular change on the pore structure of the material with changing acid amount since there is not an ordered increase or decrease, it is obvious to tell that acid amount has an effect on the pore structure of the product. Again, two different pore systems in terms of the pore sizes were observed. The average pore sizes are 3.4 (smaller pores) and 5.9 nm (larger pores) for 0.5 g; 3.4 and 5.9 nm for 1 g; and 3.4 and 5.1 nm for 80 ratio.

CHAPTER 4

Conclusion

In this study, it was shown that the MASA method can be used to synthesize mesoporous CdTiO₃ thin films. Several optimizations such as; the acid amount, the salt:surfactant ratio, the coating method and the determination calcination path during the synthesis have been done. It was shown that by changing these parameters pore size, surface area, purity and crystallinity of the mesoporous CdTiO₃ can be controlled.

The structure of final mesoporus film is directly affected by the meso-order of fresh films. Therefore, the observations on the fresh films are crucial to obtain an ordered mesophase at the early stages of film preparation to have a good groundwork for later stages. The results on the fresh films showed that under certain conditions, the formed mesophase can keep a high amount of salt between the surfactant domains for up to 2 days, which is an extraordinary property. By TEM and SEM images, it was shown that the synthesis of a mesoporous CdTiO₃ film was achieved. The only side product forming during the synthesis was found to be CdO crystals. The starting temperature for calcination process was determined to be 150°C. The mesostructured is stable up to 550°C and above this temperature the material collapses and undergoes crystallization and growth into a crystalline bulk CdTiO₃ phase. Compared to drop casting and spin coating methods, dip coating method was determined to be a more effective method to coat the glass film substrates to produce more uniform films and a material containing less side products. It was shown that the salt amount of the films prepared using dip coating method can be increased to high salt:surfactant (80:1) ratio, which is advantageous to synthesize thicker CdTiO₃ walls. The BET surface area of the 20:1, 50:1 and 80:1 ratio (salt:P123 mole ratio) samples has been found to be 44, 53 and 59 m²/g, respectively. The BJH pore sizes of the same samples are 3.4, 5.9 and 3.5 nm, and the corresponding pore volumes are 0.13, 0.11 and 0.13 cm³/g, respectively. It has been seen that the amount of acid in the initial solution is important to stabilize the initial mesophase. The

fresh samples prepared with low amount of acid leached out salt crystals in a shorter time compared to the ones prepared with higher amounts of acid. In order to find the optimum amount of acid for the initial solution and observe the effect of pH on the mesoporous structure, The sample containing 50:1 salt:P123 ratio prepared using 0.5, 1 and 2 g acid have 78, 53 and 73 m²/g BET surface area, 5.9, 5.9 and 3.5 nm pore size and 0.18, 0.11 and 0.14 cm³/g pore volume, respectively.

Overall the MASA method is an effective way of making mesoporous CdTiO₃ thin films prepared with dip coating method and having 50:1 salt:P123 mole ratio which was produced from an initial solution containing 0.5 g acid.

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