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Crystal Growth Study of CoZnPO-HEX (CZP) Synthesised Using Solvent-Free Method and Its Theoretical Simulation

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Abstract

Zincophosphate having a CZP structure (CoZnPO-HEX) has potency as a catalyst in Knoevenagel condensation of benzaldehyde with activated methylenic compounds or the Michael addition of nitroethane to olefin. The potency is led by the physicochemical properties of the material, which depend on its crystal habits. Understanding the crystal growth of materials is important to be able to design and control their crystal habits. Therefore, the crystal growth study of CoZnPO-HEX is crucial for its crystal habit modification as well as for optimization and expansion of the material's functions. Several parameters of crystal growth, such as nucleation time, gel supersaturation, and crystal size changes during the synthesis process can be analysed by observing the material's crystallisation profile. In this study, crystallisation analysis was performed on CoZnPO-HEX, synthesised using the solvent-free method, from its crystallinity curve based on Powder-XRD data supported by SEM data. As a comparison, crystal growth simulation was performed using CrystalGrower program to determine the morphology, surface topography, and theoretical crystal growth mechanisms. From this study, we found that the nucleation time of the CoZnPO-HEX crystals prepared using a solvent-free method took place during the precursor grinding process at room temperature. The crystal morphology of the as-prepared materials agrees well with the simulation's one. Moreover, the CrystalGrower simulation proved that the smallest t-czp-1 tile started the nucleation on the crystal surface because of its low free energy.

Keyword: *CoZnPO-HEX, CZP, crystallization curve, crystal growth*

Abstrak

Zinkofosfat dengan struktur CZP (CoZnPO-HEX) memiliki potensi sebagai katalis dalam reaksi kondensasi Knoevenagel dari benzaldehida dengan senyawa metilen aktif atau reaksi adisi Michael dari nitroetana ke olefin. Potensi ini dimungkinkan oleh sifat fisikokimia materialnya, yang tergantung pada crystal habits-nya. Memahami pertumbuhan kristal (crystal growth) suatu material penting untuk desain dan kontrol crystal habits. Oleh karena itu, studi pertumbuhan kristal CoZnPO-HEX sangat penting dilakukan untuk modifikasi crystal habits kristalnya serta untuk optimalisasi dan pengembangan fungsi material tersebut. Beberapa parameter pertumbuhan kristal, seperti waktu nukleasi, supersaturasi gel, dan perubahan ukuran kristal selama proses sintesis dapat dianalisis melalui profil kristalisasi material tersebut. Dalam studi ini, analisis kristalisasi dilakukan pada CoZnPO-HEX, yang disintesis menggunakan metode solvent-free, berdasarkan kurva kristalinitasnya yang dibuat dari data Powder-XRD yang didukung oleh data SEM. Sebagai perbandingan, simulasi pertumbuhan kristal dilakukan menggunakan program CrystalGrower untuk menentukan morfologi, topografi permukaan, dan mekanisme pertumbuhan kristal secara teoretis. Dari studi ini, diketahui bahwa waktu nukleasi kristal CoZnPO-HEX, yang disintesis menggunakan metode solvent-free, terjadi selama proses penggerusan precursor pada suhu kamar. Morfologi kristal hasil sintesis sesuai dengan hasil simulasi. Selain itu, simulasi CrystalGrower membuktikan bahwa tile terkecil, yaitu t-czp-1, yang berperan untuk memulai nukleasi pada permukaan kristal karena energi bebasnya yang rendah.

***Kata Kunci**: CoZnPO-HEX, CZP, kurva kristalinitas, pertumbuhan kristal.*

I. INTRODUCTION

Zincophosphate (denoted as ZnPO) was synthesized for the first time by Meier and Stucky in the early 1990s [1]. This material has a framework structure like that of zeolites composed of tetrahedra [PO4] and [MO4] (M = metal atoms) [2]. This zeotype material has potency as a catalyst, ion separation [3], and adsorption [4]. Just like zeolites, zincophosphate has been modified to suit certain applications [5]. Modifications on porous materials such as zeolites and zeotypes are carried out to obtain materials with high reactant/product selectivity based on their pore architecture and chemical composition [6], [7].

The CoZnPO-HEX was first prepared by Rajic and coworkers (1995) [8] by substituting Co(II) atoms into the hexagonal zincophosphate framework. The synthesis was carried out by hydrothermal method at 50°C for 1 hour and produced two phases of zincophosphate: zincophosphate with sodalite structure (SOD) and hexagonal phase of CoZnPO [8]. In 2010, Liao and co-workers [4] modified the synthesis method of CoZnPO-HEX with the solid-state method at 60°C for 6 hours with the addition of Polyethylene Glycol 400 (PEG-400) as an anionic surfactant. The addition of surfactants directs the polymerization process so that pores of the desired size are formed [9]. From that synthesis method, Liao et al. (2010) [4] successfully synthesized CoZnPO-HEX with only a hexagonal phase presented. However, from these two studies of CoZnPO-HEX synthesis methods, crystal growth analysis of the material has not been carried out.

Crystal growth analysis is carried out to explain what events occurred during the crystal synthesis process. An understanding of crystal growth allows control of crystal habits (morphology, crystal size) and crystal defects [10], [11]. Control of the size and morphology of the crystals will produce porous materials with new designs and functions that are adapted to their applications [12]. Cheetham et al. (1999) [1] observed that nanoporous UTD-1 with lattice defects had very good catalytic activity, adsorption properties, and mechanical stability. Zeolite A with round edges on its cubic crystals is more favorable for detergent builders as the sharp edges [13]. In a separate report, Mitchell et al. (2012) [14] suggested that carrier characteristics (size, morphology, surface properties) are crucial in the delivery process as they affect the biodistribution of the carrier, internalization in the body cells, and its clearance from the body.

Crystal growth analysis can be done with different techniques. The crystallization curve from XRD data shows growth parameters, such as nucleation time, gel supersaturation, and crystal size changes, during the synthesis. More advanced techniques of crystal growth analysis using Atomic Force Microscopy (AFM) have been reported to study real-time crystal growth on nanoporous materials [15], [16], [17].

Open-frame zincophosphates with CZP (including CoZnPO-HEX) and Faujasite (FAU) framework structures have interesting properties in catalytic reactions, such as the condensation of Knoevenagel benzaldehyde with methylene compounds or the addition of Michael nitroethane to olefins. Therefore, crystal growth studies on the materials need to be carried out to optimize and expand the functions and applications of the material.

In this report, crystallization analysis of CoZnPO-HEX (CZP framework structure) was synthesized using a solvent-free method. Crystallization analysis was based on a crystallinity curve created from Powder-XRD (PXRD) data supported by Scanning Electron

Microscopy (SEM) data. Crystal growth simulation using CrystalGrower software was carried out to theoretically explain the morphology, surface topography, and mechanism of CZP crystal growth on a molecular scale. CrystalGrower is a software for simulating crystal growth based on the Monte Carlo method which can explain crystal habits and crystal surface topography nanoscopically at equilibrium conditions [18]. This software has been successfully used to simulate crustal growth of zeolites and zeotypes (such as LTA, FAU, UOV, NES, MFI, ETS-10 frameworks), metallophosphates (such as CHA and AEI frameworks), Metal Organic Frameworks or MOFs (such as HKUST-1 and MOF-5), as well as protein (L-cystine and D-cystine) [10].

II. METHODOLOGY

The synthesis of CoZnPO-HEX by the solvent-free method modified the synthesis procedure by Liao *et al*. (2010) [4]. Zinc sulfate heptahydrate (Merck) and cobalt chloride (Merck) were mixed with $Na_3PO_4.12H_2O$ (Merck), and then PEG-400 was added to the mixture and ground using mortar for 20 minutes. After that, the mixed gel was heated at a temperature of 60 °C for 0, 0.5, 1, 2, 4, and 6 hours. The synthesized gel was washed with a small amount of distilled water and 96 % ethanol and then dried at 100 °C for 2 hours. The sample codes are written in Table 1.

Table 1 Sample codes

Sample	Heating time (h)
CZP-S0	0
CZP-S0.5	0.5
CZP-S01	1
CZP-S02	2
CZP-S04	4
CZP-S06	6

Samples were characterized using PXRD and SEM. PXRD analysis was performed using an X-ray of Cu K_α with a wavelength of 1.5418 Å and angle range 2θ = 3–50°. The crystallinity percentage of the sample was calculated based on Wang *et al*. (2007) [19], *i.e*. determined by dividing the peak intensity of each sample by the highest peak intensity at around $2\theta = 11.7°$ and multiplying it by one hundred percent (*Equation* 1). The crystallinity percentages were then plotted as a function of synthesis time into a crystallinity curve. Moreover, SEM analysis was carried out at a magnification of up to 100,000 times.

$$\%\ \text{Crystallinity} = \frac{\text{peak intensity at } 2\theta{=}11.7° \text{ of each sample}}{\text{peak intensity at } 2\theta{=}11.7° \text{ of CZP-S04}} \times 100\% \qquad (\textit{Equation } 1)$$

For the crystal growth simulation, the CZP CIF file was converted into Natural Building Units (NBU) using *ToposPro* software. The result is a VIS file which is used to analyse the crystal growth of CoZnPO-HEX using the *CrystalGrower* program. CZP crystal growth parameters run in this study were set as follows. The iteration was set to 10,000,000 with $\Delta\mu_1$ = 100.0 kcal.mol^{-1}. The energy of each tile was: *t*-czp-3 = 1.8 kcal.mol^{-1}; *t*-czp-2 = 2.5 kcal.mol^{-1}; *t*-czp-1 = 1.8 kcal.mol^{-1} and reaches equilibrium at $\Delta\mu$= 10.86 kcal.mol^{-1}.

III. RESULTS AND DISCUSSION

Figure 1 shows the diffractograms of CoZnPO-HEX samples which confirmed the high degree of crystallinity of the samples. The diffractograms confirmed that the synthesized sample is pure CoZnPO (CZP framework structure). There is a shift in the 2θ of CZP-S0, CZP-S0.5, and CZP-S01 peaks which may be associated with the different batches of synthesis. CZP-S0 has shown some degrees of crystallinity although amorphous phase diffractions are seen. This indicates that the CoZnPO-HEX nucleation process occurred during the grinding process. This peak intensity continued to increase until the heating time was 4 hours.

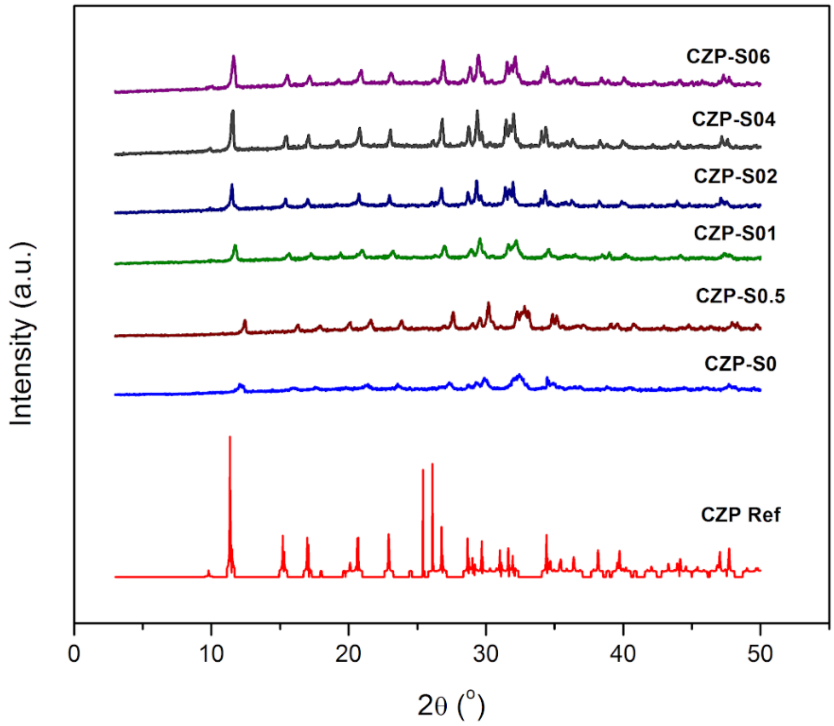

Figure 1. Diffractograms of CoZnPO-HEX synthesised using a solvent-free method

SEM analysis of the CoZnPO-HEX sample synthesized using a solvent-free method reveals an elongated hexagonal dipyramid as shown in Figure 2. The morphology from this synthesis is uniform and is similar to that of the crystals prepared hydrothermally by Rajić, et al. (1995) [8], which have a prismatic morphology with a crystal size of up to 50 μm. However, the crystal size resulting in this study is much smaller than that of Rajić's.

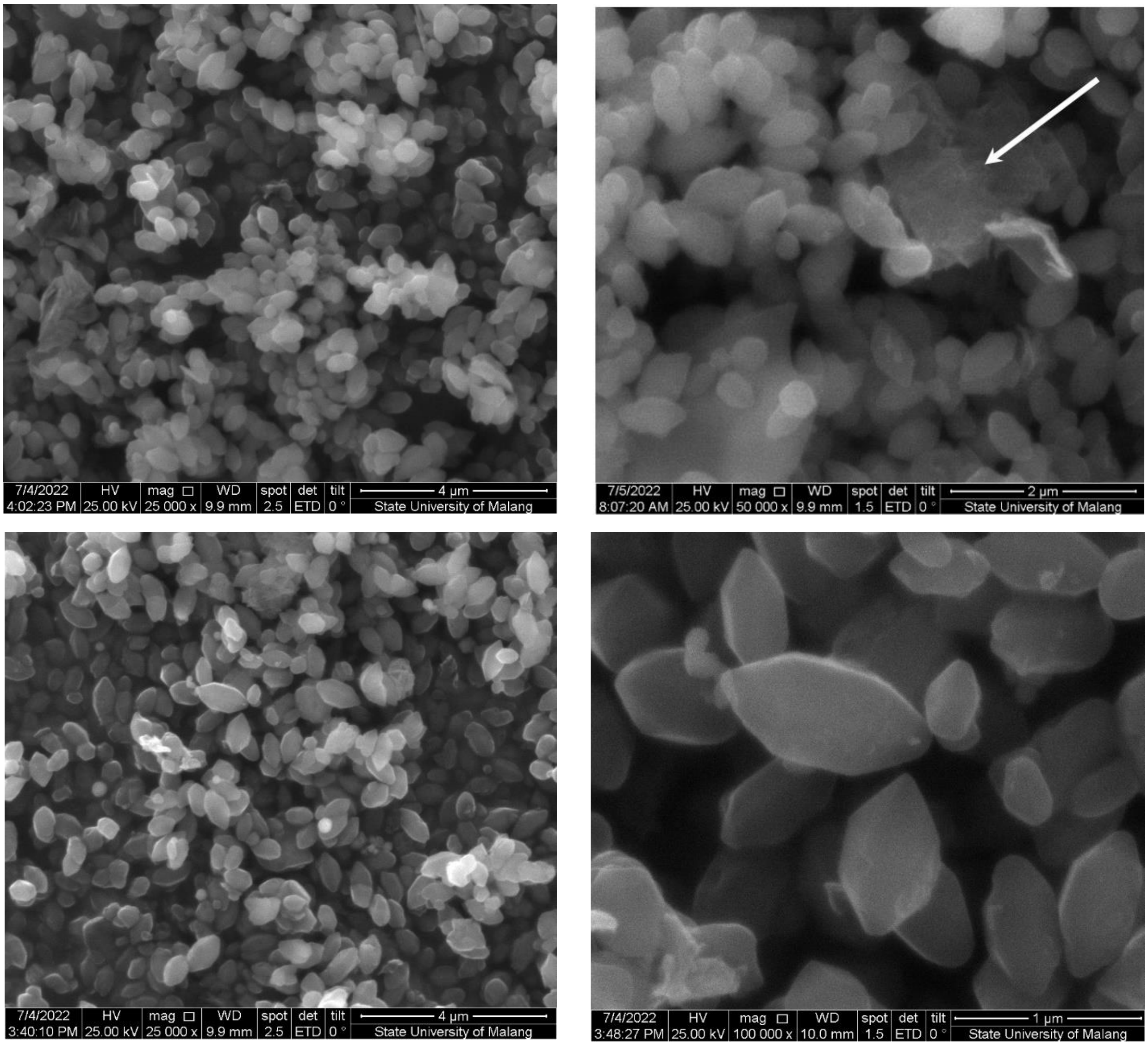

Figure 2. SEM images of (top position) CZP-S0 and (bottom position) CZP-S06

The crystals of the CZP-S0 sample have a blunt end with a length of less than 1 μm and a diameter of less than 500 nm. Longer heating in the preparation procedure results in crystals with sharper ends, longer dipyramids (up to more than 1 μm), and larger diameters (CZP-S06). It means that during the precursor grinding process, the CZP crystals have formed but with a low crystallinity degree with the presence of an amorphous phase indicated by white arrows. This SEM analysis is in good agreement with the XRD data.

The crystallinity percentages of the samples from PXRD data at various solvent-free synthesis times were then plotted into a crystallinity curve shown in Figure 3. Based on the curve, the induction time of CoZnPO-HEX during the solvent-free synthesis takes place just after the mixing of the precursors and before the gel is heated. Furthermore, the nucleation is possibly initiated before the heating process until a few minutes after the heating starts. The percentage of crystallinity, and so does the crystal size, of CoZnPO-HEX samples continue to increase with increasing crystallization time until 4 hours of heating. Thus, we can assume that the supersaturation of the synthesis gel, based on the typical nanoporous material synthesis process [11], reaches its maximum until 4 hours of heating at 60 °C and begins to decrease afterward. This occurs as the nutrients for the growing process in the synthesis gel begin to run out. In this condition, the crystal size begins to stop growing along with the depletion of nutrients for crystal growth in the mixture. The small crystal size produced using the solvent-free synthesis method (Figure 2) is a sign that during the nucleation process, the gel forms more nuclei than that of the hydrothermal method. Hence, fewer nutrients are available for growing the crystal leading to a smaller crystal size.

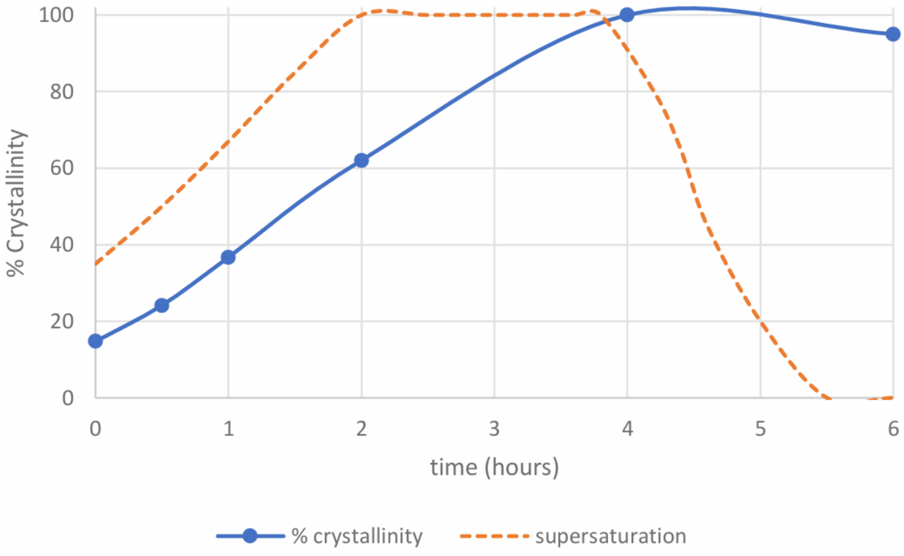

Figure 3. Crystallinity curve CoZnPO-HEX prepared by solvent-free method

CZP crystal structure simulations were carried out using *CrystalGrower* with the energy of each tile set as follows: *t*-czp-3 = 1.8 kcal.mol^{-1}; *t*-czp-2 = 2.5 kcal.mol^{-1}; and *t*-czp-1 = 1.8 kcal.mol^{-1}, with $\Delta\mu 1$ = 100 kcal.mol^{-1} and reaches equilibrium at $\Delta\mu$= 10.86 kcal.mol^{-1}. The simulation result is presented in Figure 4 and agrees very well with the results of the SEM analysis as shown in Figure 2.

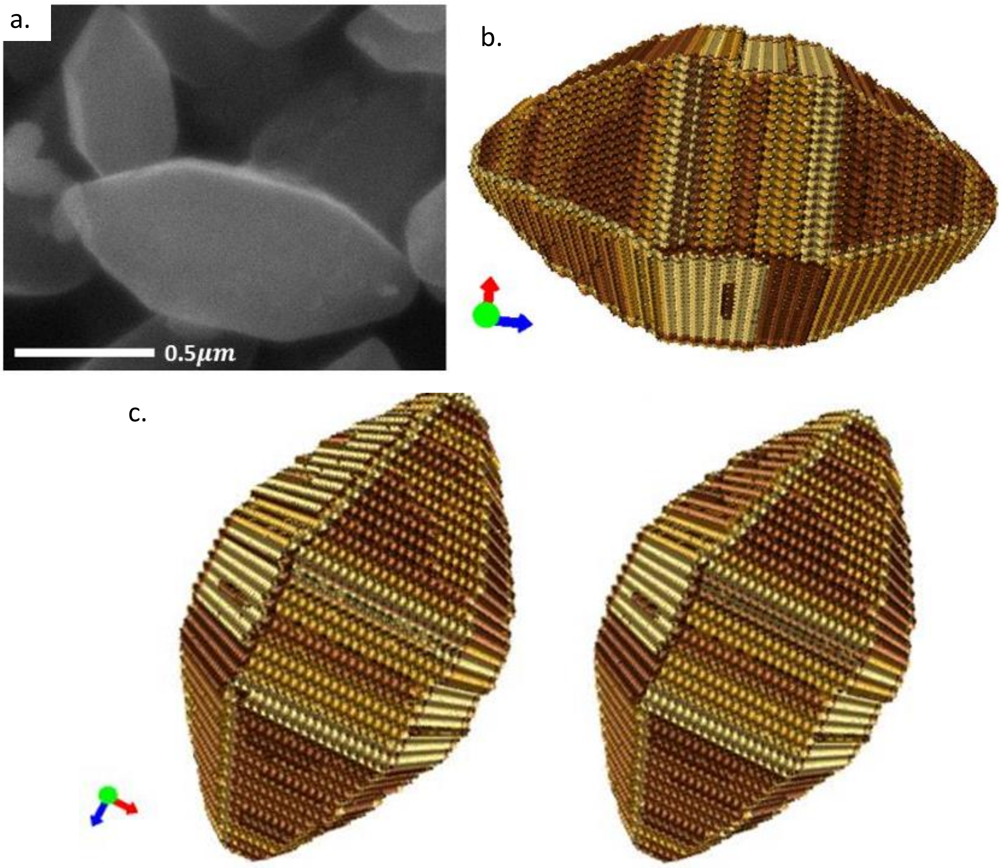

Figure 4. (a) SEM images CoZnPO-HEX sample; (b) CZP crystal growth simulation using *CrystalGrower* program observed using *CG Visualiser*; (c) and mechanism of CZP crystal growth on the longitudinal area of the facet (011) as seen from (001)

The mechanism of CZP crystal growth on the longitudinal area of the facet (011) is shown in Figure 4(c). The unit growth attaches to the crystal surface step-by-step until forms a step monoatomic layer. Therefore, the mechanism of CZP crystal growth is layer by layer. Figure 5 shows a closer look at the facet (001) on the crystal surface. Core growth on the surface of the CZP crystal starts from tile *t*-czp-3 (green) to *t*-czp-2 (yellow) which is indicated by the red dotted line. These two tiles form double-4-rings in structure. Symbol (*) shows that the layers are arranged step-by-step growth units onto the crystal surface. New nucleation was also found on the crystal surfaces (*) and (**) in Figure 5. Nucleation in this crystal surface model was seen starting from small tiles (*t*-czp-1) and followed by large tiles (*t*-czp-2) on the terrace to build the crystal surface structure. This is because the *t*-czp-1 (purple) tile is connected to three other atoms which are tetrahedral coordinated (Q^3). Thus, the *t*-czp-1 tile has a high stability energy [10].

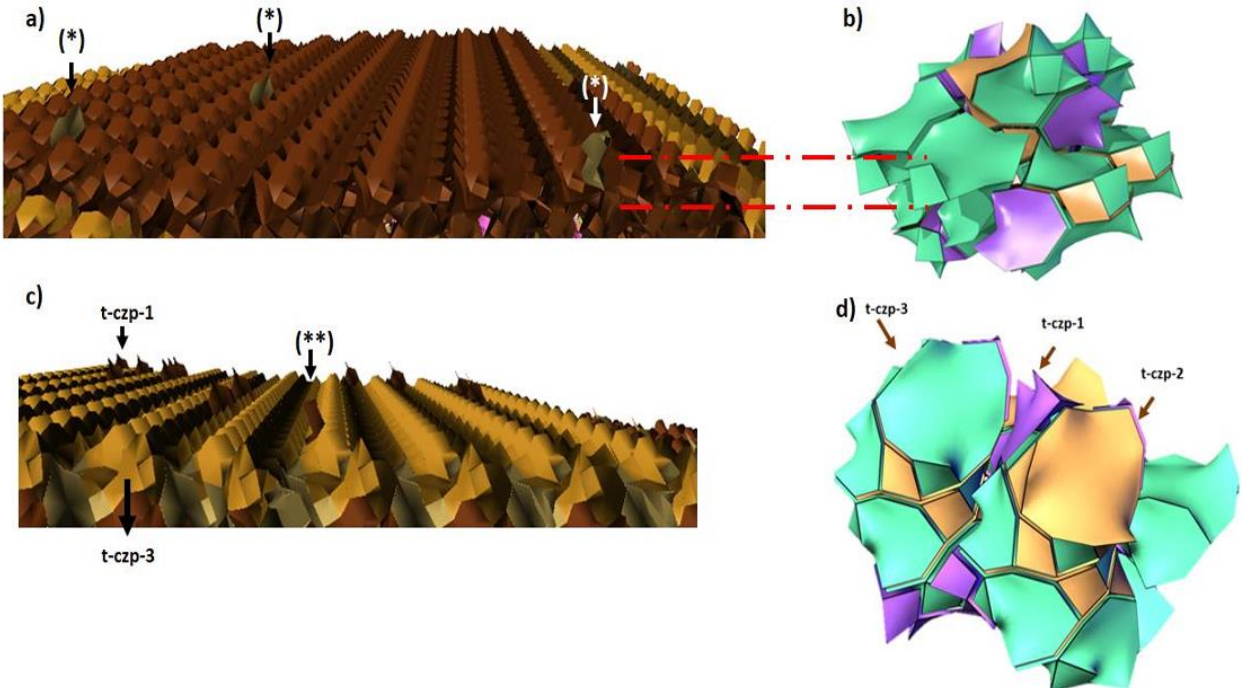

Figure 5. a) Simulation of CZP crystals on the facet (001), (*) t-czp-1 tile attached to the (001) surface; b) and d) tilling of CZP structures using *Gavrog 3dt*; c) (**) t- czp-2 tiles on the (001) surface

IV. CONCLUSIONS

Analysis of the crystal growth of CoZnPO-HEX synthesised using the solvent-free method was successfully carried out using PXRD data on various synthesis times which is then plotted into a crystallinity curve. Based on the curve, CoZnPO-HEX induction time and nucleation using a solvent-free synthesis method occurs during the grinding process before heating. SEM results revealed an elongated hexagonal dipyramid morphology. Simulation with *CrystalGrower* agrees with the experimental results. CZP crystals grow with a layer-by-layer growth mechanism with the direction of crystal growth on the facet (111). CZP crystals reach equilibrium at a supersaturation of $\Delta\mu$ = 10.86 kcal.mol^{-1}.

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