



**Controllable Solute-Diffusion Gel-Growth of BCHT: An Effective Approach Towards Large Functional Material Single Crystal Synthesis**

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## ARTICLE

# Controllable Solute-Diffusion In-Gel Growth of BCHT: An Effective Approach Towards Large Functional Material Single Crystal Synthesis

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An underutilized, but highly advantageous, method of growing functional single crystals, the in-gel growth method, is reported here. This method enables precise control of solute-diffusion, allows crystals to be grown at ambient temperatures and facilitates a lower concentration of material defects. Furthermore, the in-gel growth method creates preferable stable growth conditions where the effects of gravity are well-balanced by buoyancy effects. This makes it an analogous method to growing crystals in microgravity conditions, thus eliminating the impact of convection on crystal growth. In this study, large (cm), nonlinear optical crystals, Bismuth Chloride Hydrate Thiourea (BCHT), were successfully grown as a model material system using the double-diffusion gel growth method. Atmosphere-dependent and temperature-dependent in-situ X-Ray diffraction were used to study the phase change of as-grown BCHT crystals, revealing a step-by-step dehydration process towards the anhydrous  $\beta$ -bismuth thiourea chloride (BTC) phase when exposed to air. The elemental and structure properties of the stable anhydrous  $\beta$ -BTC phase were further investigated using time of flight secondary ion mass spectroscopy and micro-computed tomography techniques. The presented results demonstrate that, after the BCHT dehydrates to  $\beta$ -BTC, a complex network of low-density defects is present.

**Keywords:** Gel-growth, Crystallinity, Solute-diffusion, Single crystals, Functional Materials, Bismuth Thiourea Chloride

## Introduction

There are several crystal growth methods often used to synthesize functional single crystals including solution growth, melt growth, and vapor deposition. Among these growth techniques, solution growth is widely used for growth of large functional single crystals due to the ease of implementation and the low production cost. One of the key factors affecting the quality of as-grown crystals is the control of solutes in the crystal growth. Very often, the solution growth method is not able to provide precise solute diffusion control which could significantly limit the crystallinity and the size of as-grown crystals. Hereof, one alternative growth method which is largely underutilized is the gel growth method. In this method, reactants are initially separated by a gel matrix. These reactants then diffuse through the matrix to form the desired crystalline compound. There are many gels in which crystals can be grown including silicate gels, gelatin, and agarose<sup>1</sup>.

The gel growth method has several advantages that distinguish itself from other growth techniques. Using this method, crystals may be grown at ambient temperature resulting in lower concentrations of non-equilibrium defects<sup>1,2</sup>.

The gel medium also acts as an in-situ filter because solid particles cannot move in it, i.e. foreign particles present during gel formation are trapped in the gel walls<sup>3</sup>. Due to the transparent nature of many gel matrices, the formation and growth of crystals may be observed in real time during all stages of crystal growth. The as-grown crystals are suspended in the gel, limiting contact with the container walls and other crystals and eliminating potential growth stress and growth adhesions<sup>1,2</sup>. This method is inexpensive, scalable for mass production, and lends itself to growing various morphologies by changing a few of the growth conditions<sup>1,4</sup>. In fact, the nucleation and growth rate can be precisely controlled by adjusting gel density, gel pH, and gel age<sup>2</sup>. Suppressing the nucleation reduces the competitive nature of grain growth and increases the potential for formation of large single crystals<sup>2,3</sup>. By adjusting the gel pH, the pore size of the gel is altered and therefore the rate of diffusion of reactant is altered<sup>2</sup>. This provides an excellent approach to tailor the crystal growth process through adjustment of solute-diffusion. Another advantage of gel growth is its ability to limit convection phenomenon during the growth process. Each growing crystal is protected by the surrounding gel media and the effects of convection on growth could be essentially eliminated. This merit makes in-gel growth particularly suitable for simulating microgravity growth conditions at a much lower cost compared to expensive crystal growth trials in outer space<sup>5</sup>. On earth, gravity- and buoyancy-driven convection may significantly affect growth interface stability, cause microscopic gas/solution inclusions and

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fluctuate distribution of dopants, deteriorating crystallinity quality and leading to formation of various material defects<sup>5</sup>. In a microgravity environment the influence of convection, buoyancy, and sedimentation are all reduced, thus enabling a preferable growth condition for studying intrinsic growth mechanisms and improving crystallinity. Since gels reduce the effects of buoyancy driven convection, the gel-growth approach offers a promising method for synthesizing high quality single crystals.

Bismuth thiourea chloride (BTC) compound is an emerging nonlinear optical material for a series of opto-electronic applications. For this material system, there is one hydrate phase: Bismuth Chloride Hydrate Thiourea (BCHT), alternatively Tribismuthnonakisthioureonachloride dihydrate (TBNTNC), and three phases for anhydrous bismuth thiourea chloride:  $\alpha$ ,  $\beta$  and  $\gamma$  BTC<sup>6–8</sup>. All four of the phases have noncentrosymmetric structure and possess unique nonlinear optical (NLO) properties needed for a wide range of applications including lasers and optical systems. Another possible application for this class of materials is detection of ionizing radiation, such as charged particles detection and x-ray detection, owing to their promising dielectric properties<sup>6</sup>. The organic-inorganic hybrid compound BCHT (P1) has a high second-harmonic-generation (SHG) relative efficiency, which is about 40% of that of prevailing potassium dideuterium phosphate (KDP) crystals<sup>7</sup>. Chronologically, the beta phase (P3) was grown first in gel<sup>6</sup>. In a later study,  $\alpha$ -BTC (Cc) was grown from HCl solutions of Thiourea and Bismuth Chloride<sup>8</sup>. It was reported the phase change of BTC, i.e., from  $\alpha$  phase to  $\beta$  phase, occurs within hours of air exposure after removal from the growth solution<sup>8</sup>. An intermediate phase,  $\gamma$ -BTC, was observed at 140 °C<sup>8</sup>.

In this work, successful attempts were made to grow large (cm) functional single crystals with the innovative dual diffusion in-gel growth technique using a sodium silicate gel. BCHT compounds were used as a model material system during the gel growth experiments. Once harvested, the transition from BCHT to the anhydrous  $\beta$ -BTC phase was investigated through two forms of transient X-Ray diffraction (XRD), time of flight secondary ion mass spectroscopy (TOF-SIMS), and micro-computed tomography (Micro-CT). During the in-situ temperature dependent XRD, the temperature during the scan was increased from room temperature up to 200 °C. In the atmosphere-dependent XRD, a step-by-step dehydration process was observed when the sample was exposed to air, where fresh BCHT was transformed towards the anhydrous  $\beta$ -BTC phase. The TOF-SIMS was used to investigate the elemental composition of the samples near their surfaces, and the Micro-CT scan was used to investigate the post-transition structure of the  $\beta$ -BTC samples. The presented results showed that, after the BCHT dehydrates to  $\beta$ -BTC, a complex network of low-density defects is present.

## Experimental Methods

This study focused on growing BCHT crystals in sodium silicate gel. A sodium silicate gel is made by combining a sodium (meta) silicate solution with hydrochloric acid (HCl). In this

study, a semi-transparent gel with density of around 1.06 g/ml was desired. A series of growth runs were performed resulting in the harvest of a few single and multi-domain BCHT crystals. After a 48-hour period of gelation, the precursor solutions were placed on top of the gel and allowed to diffuse. The first precursor solution was formed by dissolving Bi<sub>2</sub>O<sub>3</sub> in 7N HCl. This was then placed in the arms of the U-Tube on top of the gel. The second reactant was made by dissolving thiourea in H<sub>2</sub>O, which was then placed in the center portion of the U-Tube above the gel. The volume of the reactants was greater than the space between the top of the gel and the top of the U-Tube. The U-Tube was isolated for the first trial – allowing the reactants to diffuse through the gels undisturbed. During the following trial, the U-Tube was placed on a hot plate for an extended period. The gel was kept at a constant temperature to eliminate the impact of slight temperature fluctuations from the surrounding environment. Interestingly, the formation of single crystals was not observed while keeping the gel at 20°C on the hot plate. Instead, crystals began growing when the gel was removed from the hot plate. To examine the effects of stoichiometry on gel formation, 24 different synthesis trials to optimize the composition of sodium silicate gels were performed. The HCl:WGS ratios and molarity were varied from 0.50 to 2.00. Following the gel optimization, more crystal growth runs were performed.

Powder X-ray Diffraction (PXRD) experiments were performed with a PANalytical Empyrean X-ray diffractometer (8° to 60°, 27.5 s/step, and 0.026° step) for a sample which was harvested a few days prior to the measurements. In-situ temperature dependent PXRD experiments were conducted using the same instrument for another fresh sample starting from room temperature (RT) up to 200 °C with a heating rate of 5 °C/min in an ambient atmosphere. The crystal sample was harvested from the gel in a glovebox and put in a vacuum-sealed container within an hour prior to the diffraction experiments. These temperature dependent PXRD experiments were designed to investigate the phase transformation from BCHT to the  $\beta$ -BTC phase. To better understand the transition from BCHT to  $\beta$ -BTC in a bulk sample, a transient atmospheric XRD measurement was performed as well. First, nitrogen (N<sub>2</sub>) gas was flown over the BCHT sample at 35 cc/min for a 20-minute period for purging purposes. Four XRD scans were taken during this period. Next, the gas was changed to compressed air. The flow rate was kept at 35 cc/min, while the measurement period for this portion of the experiment was 90 minutes. During this time, 20 scans were taken. Once these experiments were completed, the crystal was exposed to ambient atmosphere overnight in the XRD chamber. Another scan was performed the following morning.

Time of Flight – Secondary Ion Mass Spectroscopy (TOF-SIMS) analyses were conducted to investigate the elemental composition of the  $\beta$ -BTC samples near the surfaces. These were performed using a TOF SIMS V (ION TOF, Inc. Chestnut Ridge, NY) System. The surface was sputtered with 10 keV Cs<sup>+</sup> beam over 120  $\mu$ m x 120  $\mu$ m area to an average depth of 7.6  $\mu$ m. The used analysis beam was 25 keV Bi<sup>3+</sup> ions beam. The final

sputtered thickness was measured using a Dektak 150 Surface Profiler.

To gain more insight about the structure and defects of the stable BTC phase following the dehydration of the BCHT single crystal, a Zeiss Xradia 510 Versa 3D X-ray Tomography System was employed to conduct Micro-CT scan. The Micro-CT measurement was performed with an X-ray tube current of 62  $\mu\text{A}$ , a voltage of 160 kV with 360° rotation, and voxel size of 6.5  $\mu\text{m}$ . 2201 projections were taken with 7 sec exposure time.

## Results and Discussion

### Gel Optimization & Gel Crystal Growth

During the first crystal growth trial, the density of the WGS was determined to be 1.07 g/ml. After mixing, a gel formed in approximately 15 minutes. The entirety of the mixture, however, did not form a gel. There was still a small amount of liquid left in the arms of the U-Tube above the gel. This was drained off before the addition of the precursor solutions. During the second trial, the density of the WGS was determined to be 1.08 g/ml. In consequence, 5 ml of  $\text{H}_2\text{O}$  was added to the WGS to achieve a density of 1.06 g/ml. This brought the total solution volume to 365.4 ml. During the second trial, the solution remained a liquid past a period of 15 minutes. In both cases, the gel was covered and allowed to gelate for 48 hours before the precursor solutions were placed above the gel.

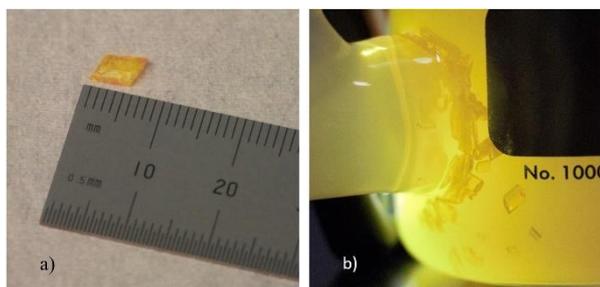


Figure 1: a) Selected crystal for measurement illustrating the 0.5 cm length b) Crystals during growth in gel.

Once started, continuous crystal nucleation and growth were observed inside the gel. At the end of the two-week growth period, the crystals were harvested from the gel. Figure

1a shows one as-grown BCHT crystal. Interestingly, it was observed that the crystals formed preferentially on the seams where the U-tube arms met the main body during the first trial (Figure 1b). This is unsurprising as this location is likely the first place where the two reactants met. Additionally, it is possible that the joints led to irregularities in the surface of the glass U-Tube which served as nucleation sites. The physical bending at the arms region may contribute to the crystal growth since it could cause perturbations in the gel density and introduce stress regions in the gel matrix making them preferential nucleation sites. After observing the hotplate growth trial, it appears that the hotplate accelerated the reactant diffusion. As a result, it was observed that as-grown crystals scattered over the gel, instead of being located only by the arms, to a greater extent than the first trial. Since the hot plate enhanced diffusion of the reactants, this supports the assumption that crystals grew around the arms because this is the location where both solutions first met. After the crystals were removed from the gel, a change in color and opacity was observed. The samples went from a semi-transparent orange color to a darker, opaque orange.

During the gel optimization trials, the solutions were examined at 15 minutes, 24 hours, 4 days, and 5 days after mixing. These results are presented in Table 1 below. Several gels formed after 15 minutes while a few solutions became a gel after 4 days of gelation. Based on this study, gel H was selected as the best candidate for the subsequent crystal growth trial because it formed a stable gel within 15 minutes and remained clear over the entire optimization testing period. Gel H corresponded to a HCl:WGS ratio of 1.00 and a molarity of 0.67. Figure 2 shows the evolution of Gel H during the optimization process.

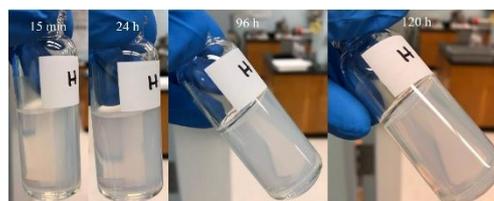


Figure 2: The evolution of Gel H at each timepoint corresponding to a HCl:WGS ratio of 1.0 and molarity of 0.67

Time	Molarity	HCl:WG Ratios				
		0.50	0.67	1.00	1.50	2.00
15 min	0.50	A	B	C	D	E
	0.67	F	G	H	I	J
	1.00	K	L		M	N
	1.50	O	P	Q	R	S
	2.00	T	U	V	W	X
24 h	0.50	A	B	C	D	E
	0.67	F	G	H	I	J
	1.00	K	L		M	N
	1.50	O	P	Q	R	S

	2.00	T	U	V	W	X
96 h	0.50	A	B	C	D	E
	0.67	F	G	H	I	J
	1.00	K	L		M	N
	1.50	O	P	Q	R	S
	2.00	T	U	V	W	X
120 h	0.50	A	B	C	D	E
	0.67	F	G	H	I	J
	1.00	K	L		M	N
	1.50	O	P	Q	R	S
	2.00	T	U	V	W	X
		Gel Formed		Somewhat Opaque		
		Clear		Opaque		
		Somewhat Clear				

Table 1: Summary of gel optimization parameters

### Powder X-Ray Diffraction & Transient Experiments

PXRD and two forms of transient XRD were performed to better understand the phase transformation from BCHT to  $\beta$ -BTC. As presented in Figure 3 and 4, the PXRD result for the fresh sample at RT matches those of triclinic (P1) BCHT<sup>7</sup>, while the PXRD of the stable phase sample matches the hexagonal (P3)  $\beta$ -BTC form<sup>8</sup>. The same dehydration phase transformation occurred around 80 °C during the in-situ temperature dependent PXRD experiment as shown in Figure 3. **Error! Reference source not found. Error! Reference source not found.**

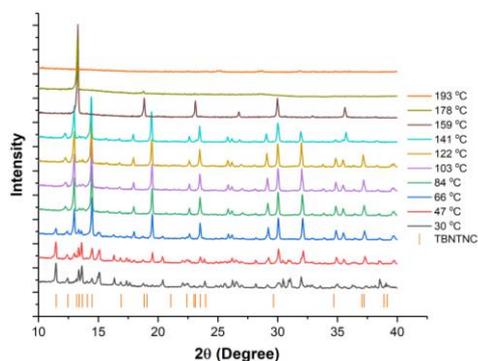


Figure 3: In-situ temperature dependent powder X-Ray diffraction (PXRD) showing phase transition from BCHT to  $\beta$ -BTC

It was observed that the start of the transformation occurs within 5-10 minutes of harvesting from the gel and is completed within a few hours. In the authors' opinion, the loss of crystallinity is mainly caused by the difference in unit cell volumes of the triclinic BCHT and the hexagonal  $\beta$ -BTC.

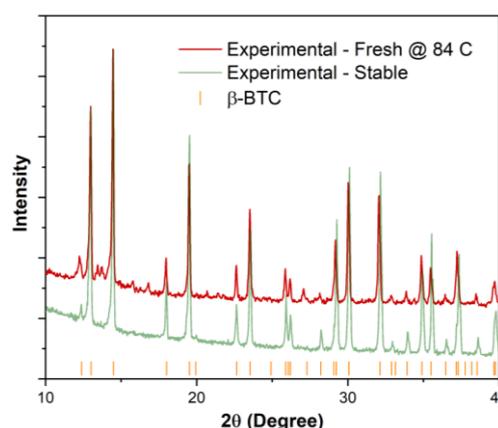


Figure 4: Powder X-Ray diffraction (PXRD) of stable phase  $\beta$ -BTC

To capture the step-by-step phase changes in fresh BCHT bulk crystal, atmosphere dependent XRD was also performed. Figure 5 shows the results of the transient atmosphere XRD experiment. As time increases, and therefore exposure to the different atmospheres, the feature diffraction peaks of BCHT can be observed to decrease significantly in intensity. This loss of peak clarity corresponds with a loss of crystallinity as the reflection from the XRD is diminished. Thus, it is revealed that, as BCHT transitions to  $\beta$ -BTC, it loses its long-range order. Interestingly, the peak around 14.5° is observed to increase with the increasing time. It appears to correspond with one of the stronger peaks present in  $\beta$ -BTC; this peak represents the (101) plane.

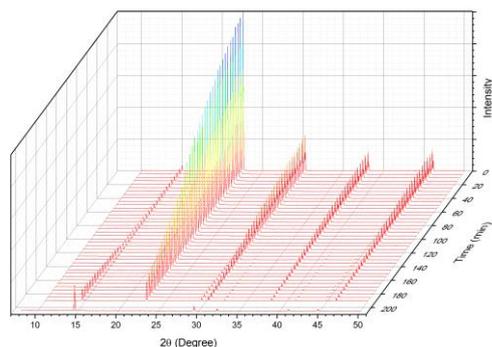


Figure 5: Transient atmosphere dependent XRD Experiment  
Time of Flight – Secondary Ion Mass Spectroscopy

Figure 6 shows depth resolved secondary ion counts, which are consistent with PXRD analysis, suggesting that the stable phase is  $\beta$ -BTC. Carbon and oxygen concentration decrease in the 2  $\mu\text{m}$  below the surface. Oxygen disappears after 3  $\mu\text{m}$  while carbon stabilizes, which may indicate that there is still a minor hydrated phase on the surface. Secondary ion counts for silicon was very low in the 2.5  $\mu\text{m}$  below the surface, and it went down to almost no counts beyond that thickness. This indicates that there is likely no silicon inclusion from the gel matrix as the crystal grows, which is in good agreement with EDX analysis for gel grown  $\alpha$ -BTC<sup>6</sup>.

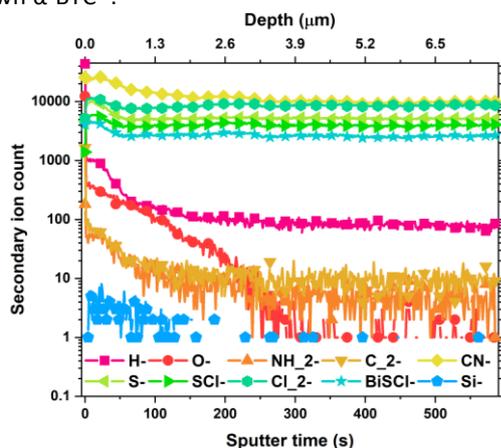


Figure 6: Depth-resolved TOF-SIMS for  $\beta$ -BTC and BCHT constituents and Si impurity

#### Micro-CT Scan

During the dehydration of BCHT single crystal to the stable  $\beta$ -BTC phase, the micro-structure is transferred from the crystalline state to an amorphous or polycrystalline state. A Micro-CT scan reveals a homogenous sample volume with a complex network of abundant low-density defects. It is presumed that these low-density defects are sub-grain boundaries, micro-cracks, or even voids, which are formed during the dehydration process. The loss of crystallinity revealed by the CT scan is consistent with the results from the transient atmospheric XRD results. By comparing these two measurement techniques, it is clear that the BCHT is formed

with higher crystal quality which then deteriorates as the crystal transitions to  $\beta$ -BTC. This indicates that the defects seen in Figure 7 are formed after the sample is removed from the gel instead of during growth.

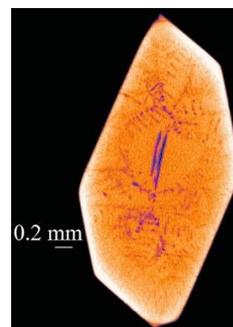


Figure 7: Cross-sectional slice of the sample from Micro-CT revealing the homogenous structure with the low-density defects.

## Conclusions

In this work, several BCHT crystal samples were grown using the dual diffusion gel growth method. After removal from the silicate gel matrix, the transition from BCHT to  $\beta$ -BTC was successfully observed both visually (through color and transparency change) and using two types of transient XRD. The dehydration phase transformation from BCHT to  $\beta$ -BTC took place by exposing the BCHT sample to ambient atmosphere and by raising the temperature above 80°C. TOF-SIMS revealed that the BCHT phase may still be present close to the surface of the sample after the bulk of the material had transitioned to  $\beta$ -BTC. Furthermore, TOF-SIMS revealed that there was little Si inclusion occurring in the samples. This is a promising result indicating that the gel matrix does not contaminate the crystal samples and can be used to grow high purity crystals. The use of Micro-CT revealed a homogeneous sample volume with an abundant, complex network of low-density defects. These defects may be sub-grain boundaries, micro-cracks or void formed when the sample dehydrated as part of its transition from BCHT to  $\beta$ -BTC.

## Conflicts of interest

There are no conflicts to declare.

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