

Mechanochemical Synthesis of Bismuth active pharmaceutical ingredients, Bismuth(III) Gallate and Bismuth Citrate.

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1. Specification of syntheses

1.1. Chemical compounds used

Tab. 1 A list of chemical compounds used in the experimentation

Compound	Purity [%]	Code	Supplier
Bi ₂ O ₃	99,999	202827-10G	Sigma-Aldrich
salicylic acid	≥99.0	105910-500G	Sigma-Aldrich
gallic acid	≥98.0	8.42649.0025	Merck KGaA
citric acid (anhydrous)	≥99.5	791725-100G	Sigma-Aldrich
citric acid monohydrate	≥99.0	C1909-500G	Sigma-Aldrich
bismuth citrate	99.999	480746-100G	Sigma-Aldrich
acetylsalicylic acid	≥99.0	A5376-100G	Sigma-Aldrich
KNO ₃	≥99.0	-	-
NH ₄ NO ₃	≥99.5	A7455-500G	Sigma-Aldrich
Acetone	≥99.5	179124-1L	Sigma-Aldrich
DMF	≥99.8	227056-1L	Sigma-Aldrich
ethanol	≥99.5	-	-
ethylene glycol	≥99.5	-	-
propanol	≥99.5	-	-

1.2. Appliances

Milling - InSolido Technologies vibration-type mill, IST500, paired with stainless steel jars (10 and 25 ml), paired with stainless steel balls (7 and 10 mm).

Diffractionmeter (1) - Bruker D2 PHASER XE-T, Cu K α radiation, zero background Si sample holders

Diffractionmeter (2) - Bruker D8 DISCOVER, Cu K α radiation, zero background Si sample holders

TGA - TA Instruments TGA Discovery, high temperature Pt sample holders

Raman spectroscopy - Renishaw inVia spectrometer, using 532 and 785 nm laser wavelengths

1.3. Mechanochemical synthesis process

Preparation of samples for each experiment started with weighing appropriate amounts of ingredients, on a balance with 0.1 mg precision. 200 to 500 mg of reaction mixture was prepared for each sample by mixing ingredients inside of the milling jars, or in a separate container, provided the jars were to be heated without the mixture. Liquid was added each time after mixing, after milling balls were placed in the milling jars. Experiments that included heating of the jars (with and without reaction mixture) used an insulated drier set to 85 °C as the heat source. It was stationed right next to the mill to ensure rapid mounting of the heated jars to the mill. The jars were each time sealed and placed inside the drier and closed for an appropriate time.

Two jars at a time were mounted onto the mill. Heated jars were mounted rapidly. Each set was milled for the same amount of time, with the same frequency, and the same set of milling balls, in order to prevent weight imbalance. After milling, samples were extracted from the jars, and placed in labeled containers for further analysis.

Depending on the expected time-sensitivity, measurements on the samples were performed right after synthesis, or after gathering a larger amount of samples.

2. Bismuth Salicylate (BiSal_2 and BiSal_3)

Fig. 1 PXRD patterns of BiSal_2 in compare to the starting materials - salicylic acid and bismuth(III) oxide.

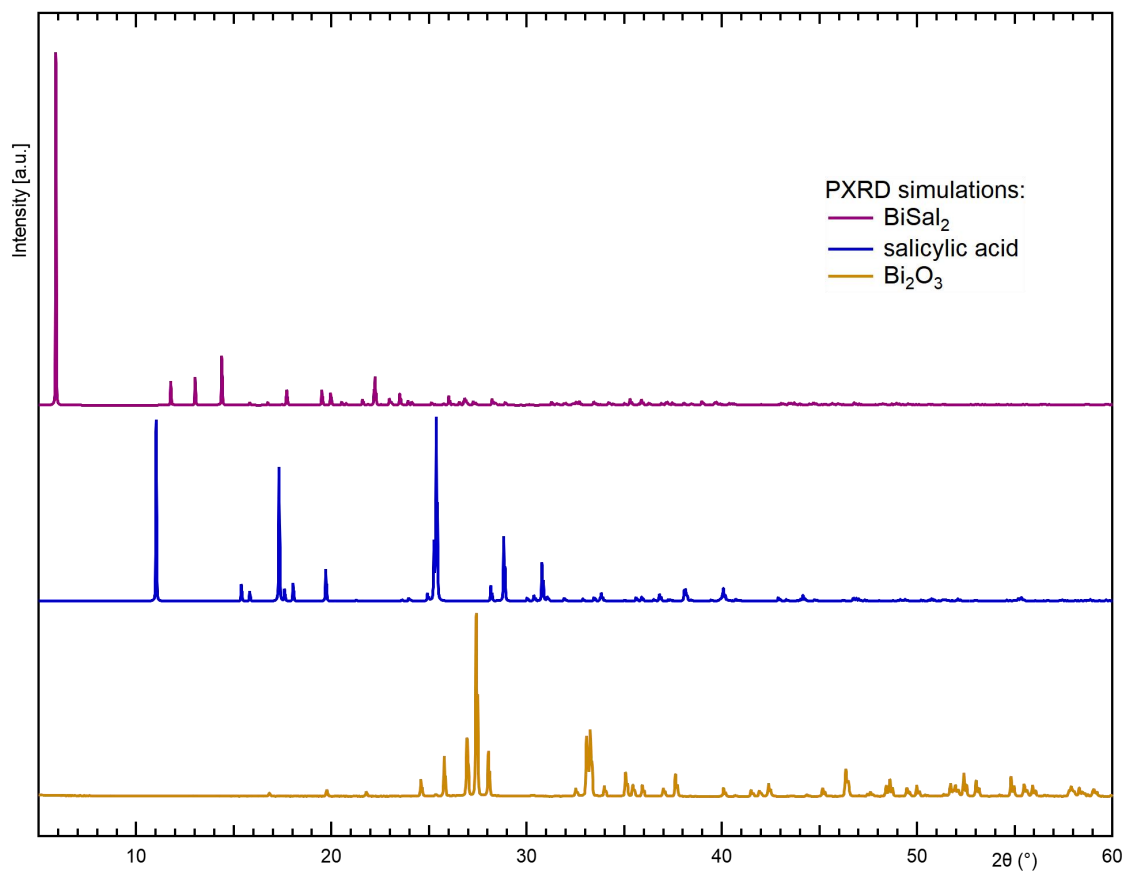


Fig. 2 PXRD patterns of BiSal₂ and BiSal₃, showing characteristic differences. First peak at around 6° and almost evenly spaced, three peaks at 11.75, 13.0, and 14.35° help distinguish BiSal₂ from BiSal₃. The latter shows first, intense peak at 8°, which can be used as a marker of BiSal₃ impurity in BiSal₂ sample.

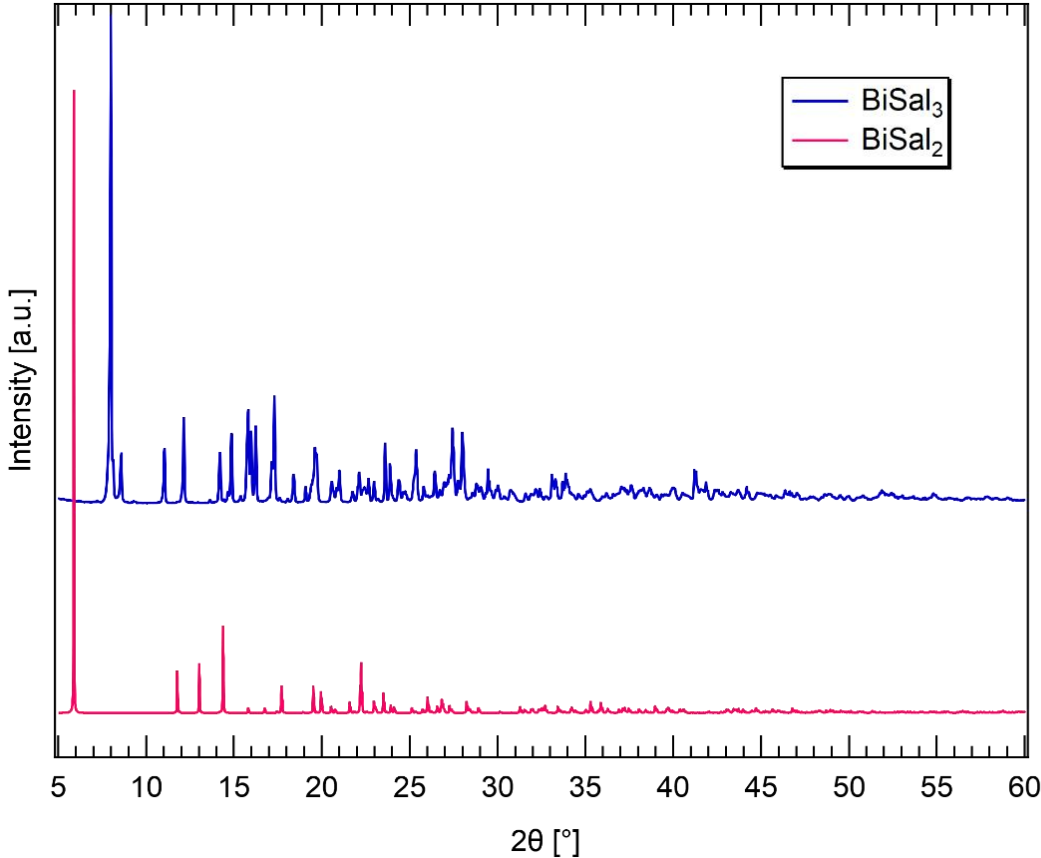


Fig. 3 PXRD patterns of bismuth(III) oxide. The „new” batch is the one, which reacts the same way that is expected based on the 2011 study, and enables BiSal_2 as a final product. The „old” batch is the one, which requires activation through heating to yield BiSal_2 , otherwise only produces BiSal_3 . Based on this comparison, there is no quantitatively significant difference in the chemical structure between the batches.

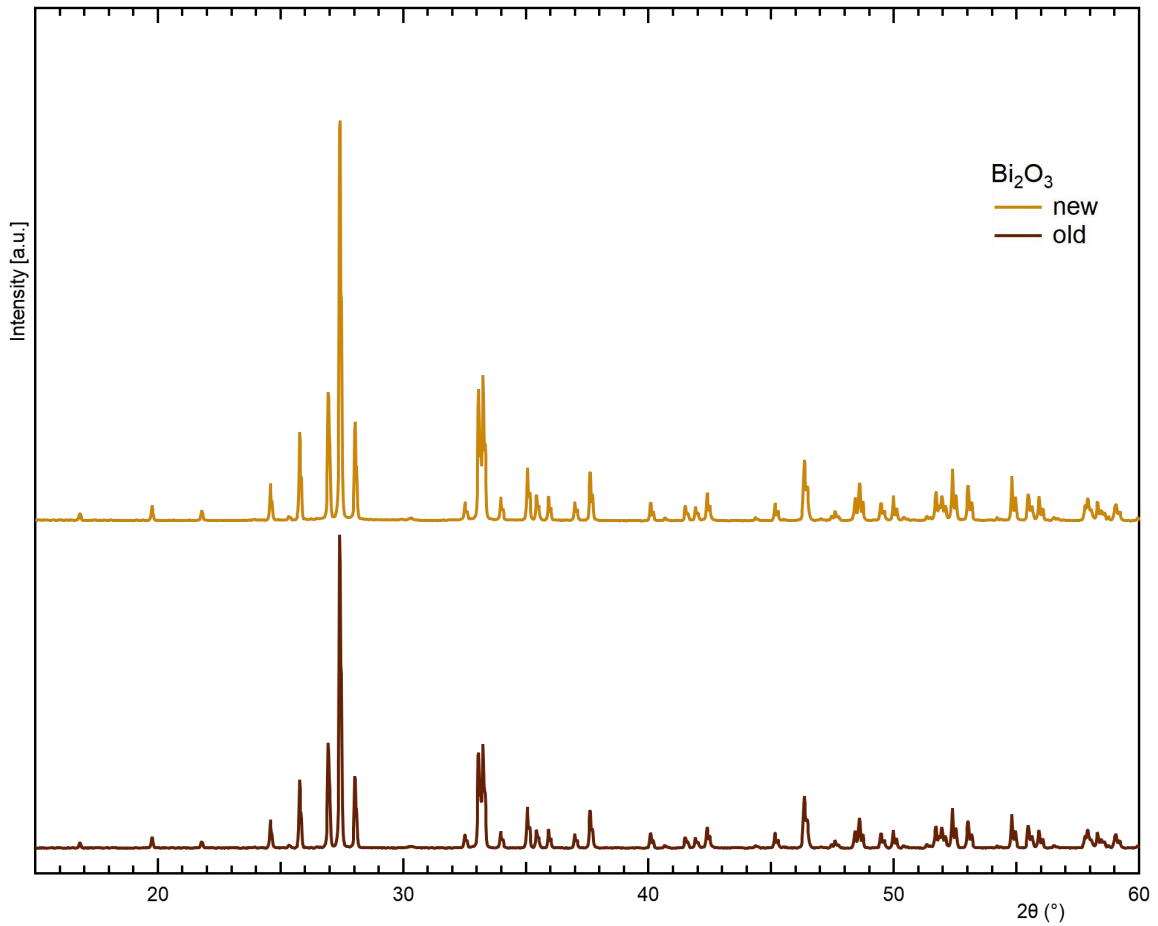
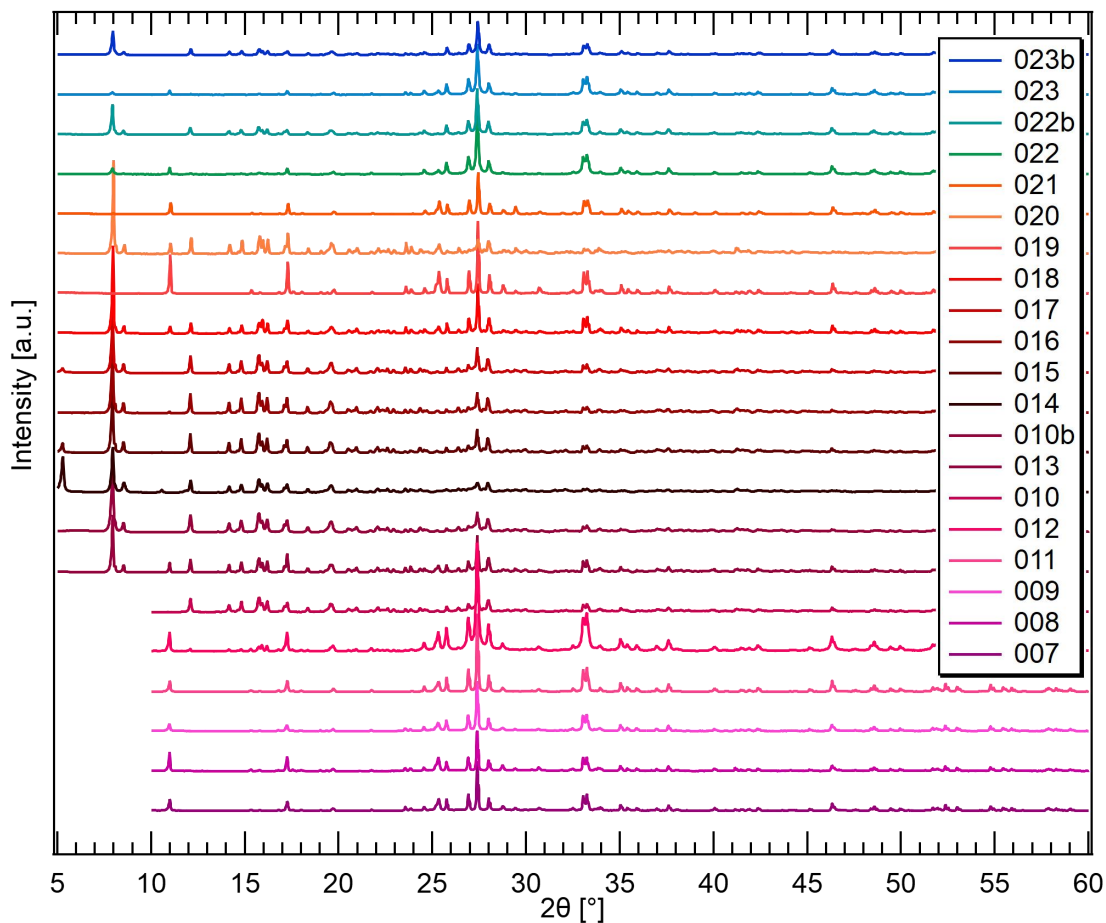


Fig. 4 PXRD patterns of some of the first samples, synthesized as a mean of obtaining BiSal₂. No traces of the compound can be found, only BiSal₃, HSal and Bi₂O₃ structures can be distinguished in the patterns. Dozens of experiments were performed, before discovering the Bi₂O₃ batch used for the synthesis was unable to react to BiSal₂, and dozens more before the synthesis of BiSal₂ was perfected. All the presented batches used the „old” Bi₂O₃, before it was discovered that it can be activated through heating in 600°C over night, and hence the respective samples were not used in final analysis to find the most suitable reaction environment.



3. Bismuth Gallate (BiGall)

The products of BiGall synthesis were measured after each mechanosynthesis using X-ray diffraction. The patterns were analyzed, looking for the purest product. The intensity of highest peak of bismuth(III) oxide (27.6°) remaining in majority of samples was compared to the bismuth(III) gallate peak next to it (26.9°) for a visual clue of a given sample purity, that was later additionally analyzed with Rietveld refinements. This then was directly used to establish the best possible result of manipulating the reaction environment.

Fig. 5 PXR patterns showing precursor materials, Bi_2O_3 and gallic acid, as well as the differences in between dry grinding, LAG and ILAG samples. Dry grinding is results in an insignificant conversion to BiGall, consisting mostly of unreacted Bi_2O_3 . However, implementing heating of the jars for 30 min in 85 °C before synthesis does improve dry grinding. LAG reaction is a significant improvement, leading close to a full conversion. Heating improves LAG slightly, similarly to using ionic salt (ILAG). Using LAG method with heating is enough to obtain BiGall, however using ILAG does improve the process in terms of reproducibility.

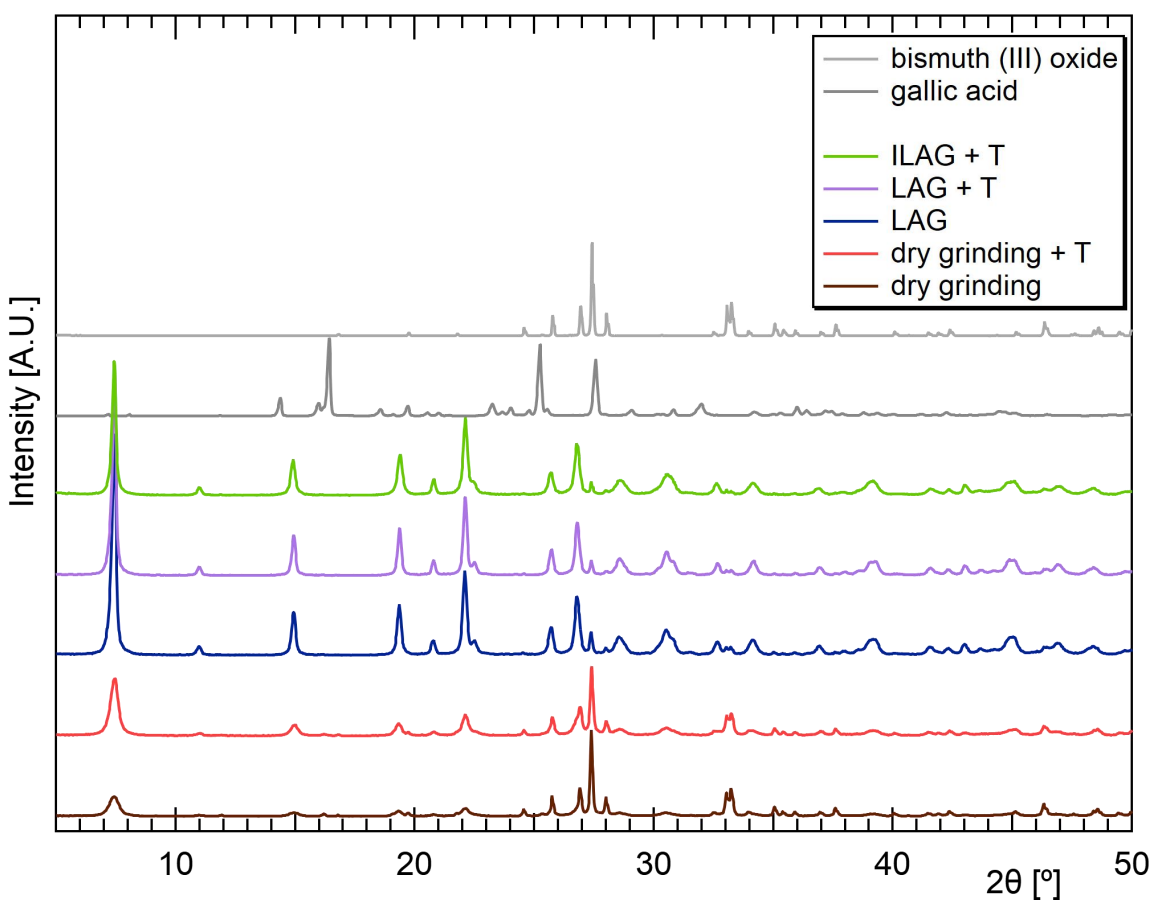


Fig. 6 PXRD patterns of BiGall samples synthesized with LAG method, using different liquids. Propanol, water, ethanol and acetone all show BiGall peaks. Acetone sample shows high content of leftover Bi_2O_3 , which we suspect to be caused by evaporation, resulting in dry grinding. Ethanol on the other hand shows a very small amount of other, unknown phase, and higher Bi_2O_3 amount than water and propanol. DMF yields an unknown product. Water and propanol are superior for LAG synthesis of BiGall.

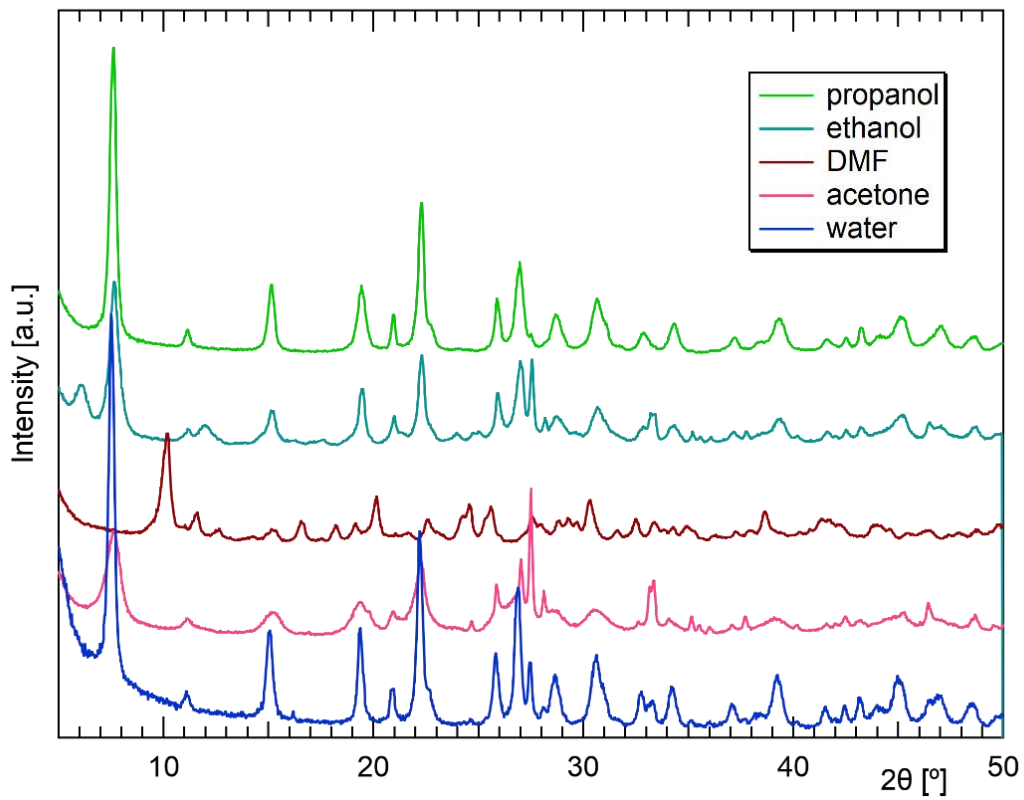


Fig. 7 PXRD diffraction patterns of two ILAG samples, synthesized with water. The 1:2 (Bi_2O_3 :HGall) ratio is superior due to the fact that the Bi_2O_3 leftover is less pronounced. The 1:4 ratio results in clearly visible HGall signal, at 12° and 16.1° , apart from more pronounced Bi_2O_3 peak at 27.6° . This results matches the stoichiometry of BiGall.

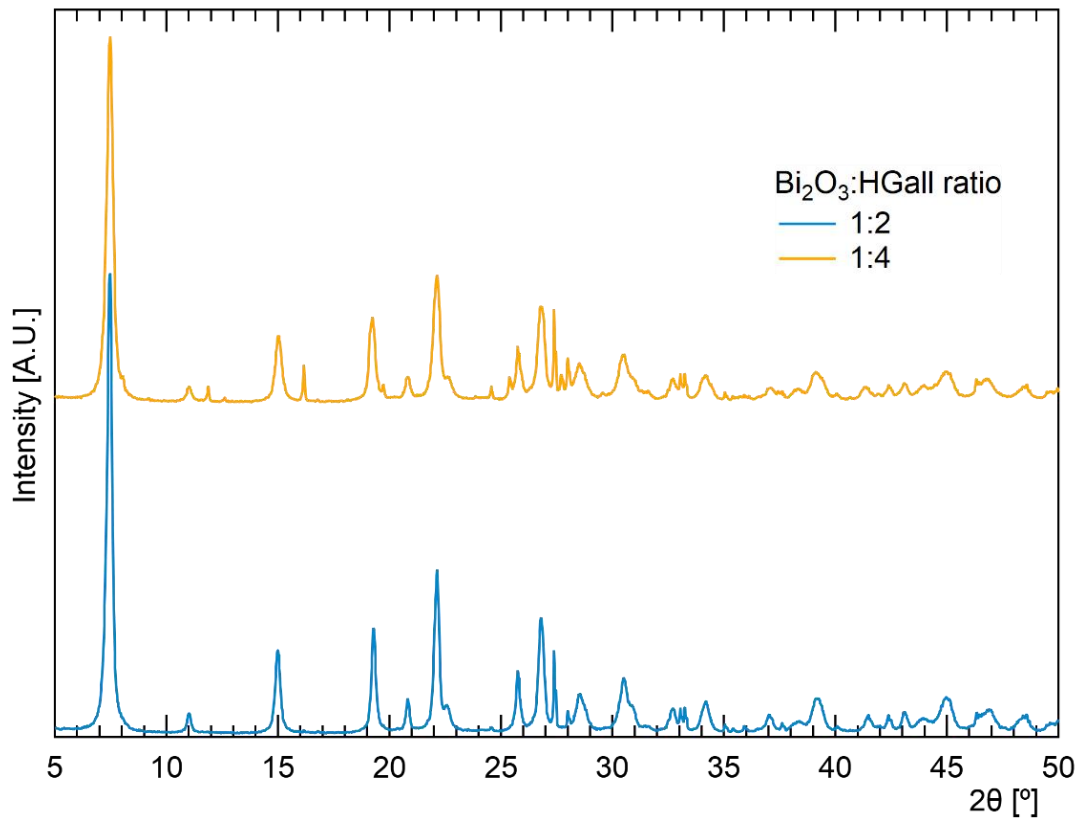


Fig. 8 PXRD of LAG samples. Here we present exploration of water-propanol mixture impact in LAG synthesis, alongside the time of grinding. Using pure water provides consistently higher conversion to BiGall, than propanol and their mixtures.

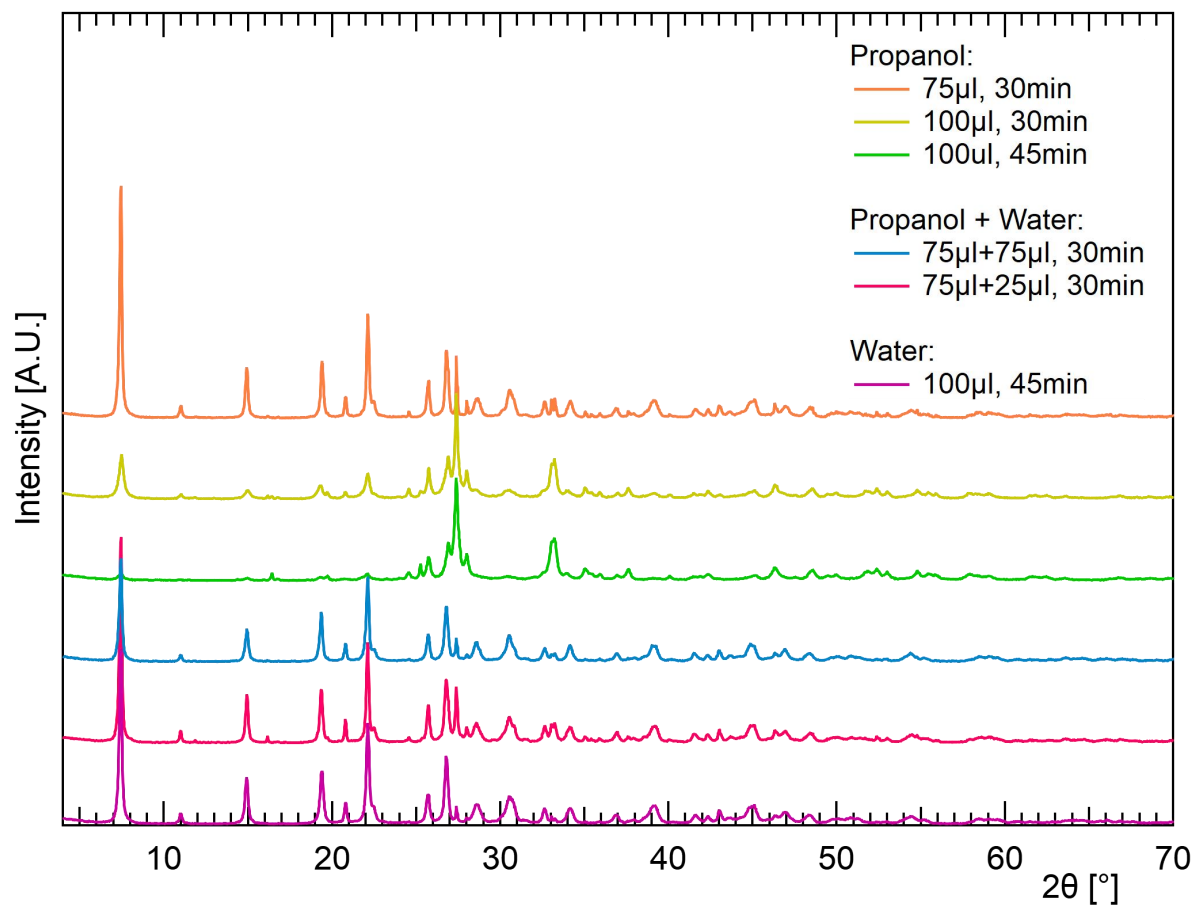
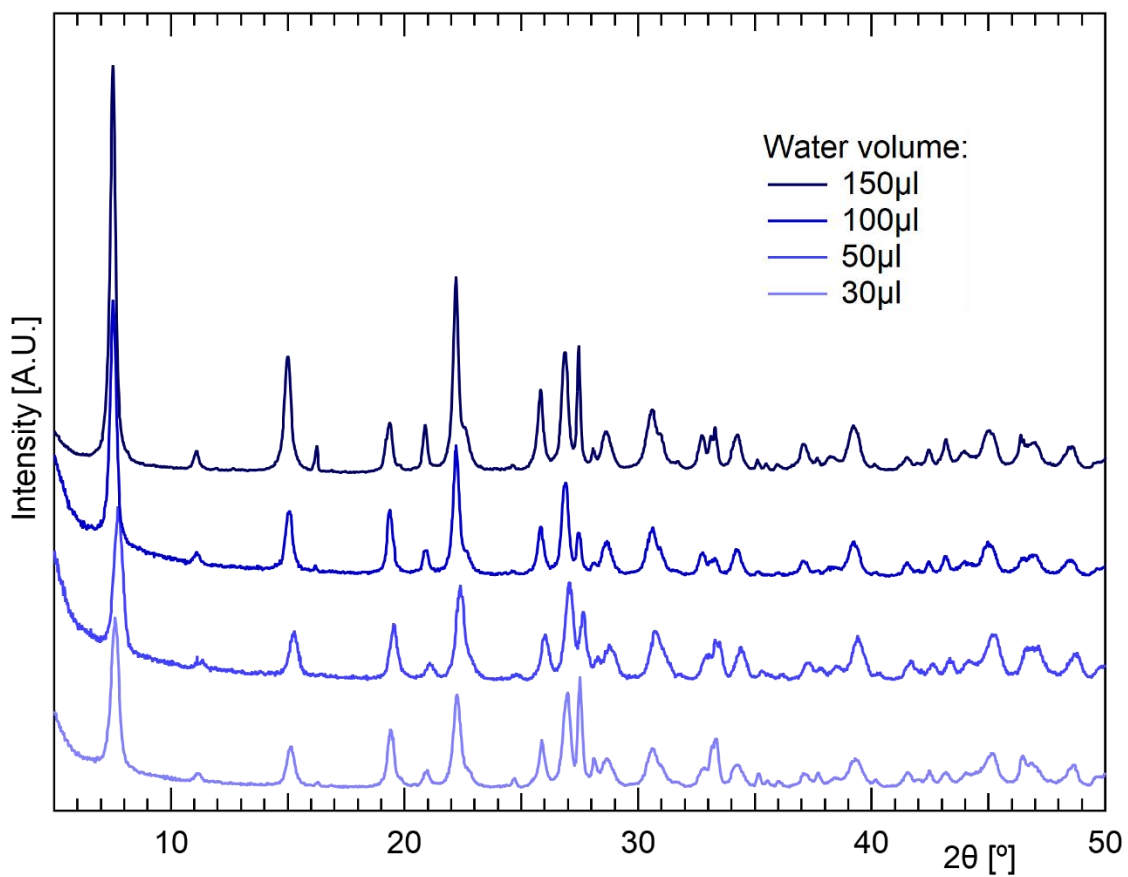


Fig. 9 PXRD patterns of ILAG samples. We present a study of influence, of the volume of water used. Use of 100 μ l per 200 mg of reaction mixture results in highest conversion.



4. Bismuth Citrate (BiCit)

4.1. PXRD

Fig. 10 PXRD patterns of relevant chemicals. Precursor materials, Bi₂O₃ and citric acid, as well as commercially available BiCit. Additionally, two mechanochemically synthesized BiCit structures, dry and wet (2a and 2b).

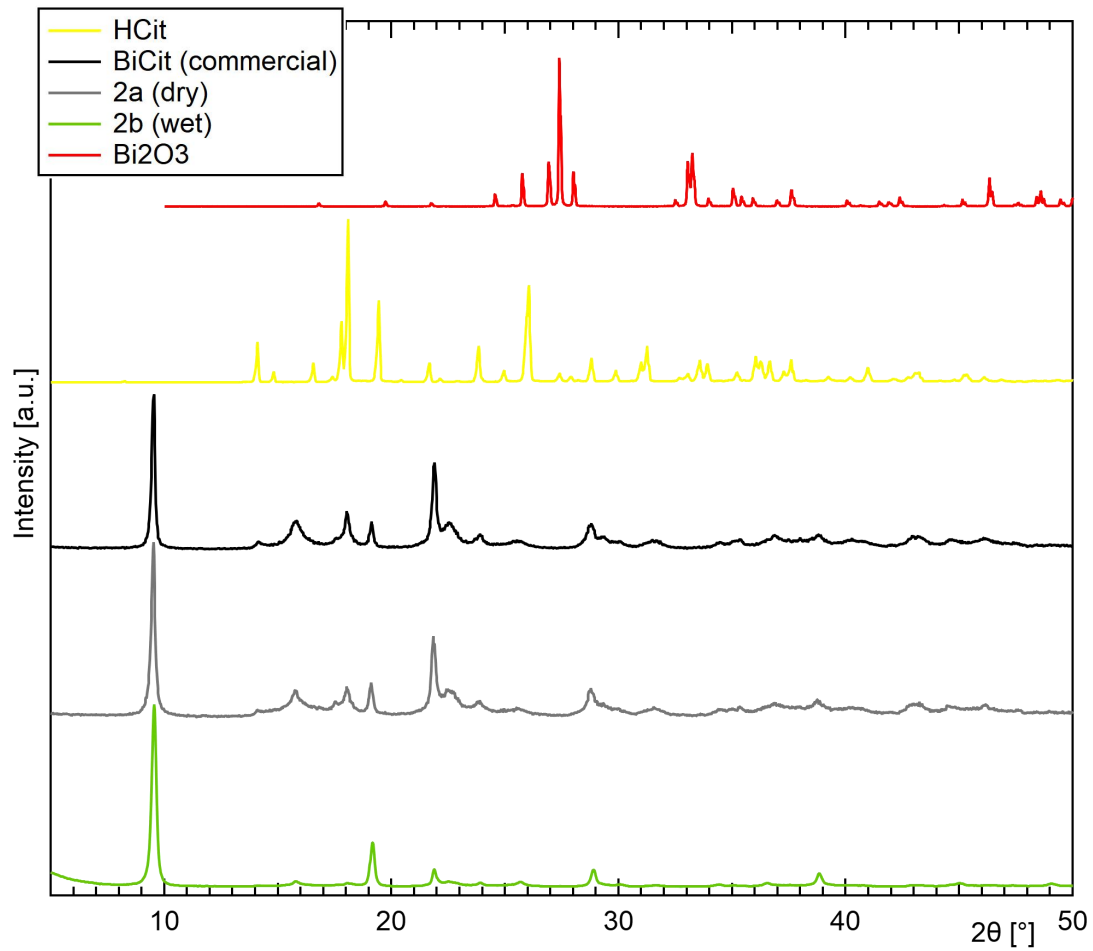


Fig. 11 PXRD patterns of aged samples, in different Bi_2O_3 to HCit ratios. The reaction mixtures, each in separate vessel, were placed in a desiccator, filled at the bottom with water. The sealed desiccator was then placed in a drier set to 60°C , for 7 days. The samples were then retrieved and let to dry. The measurements were done for dry samples, and then repeated after they were mixed with a small amount of water. All ratios are showing the change from 2a to 2b structure for all ratios, apart from the commercial BiCit.

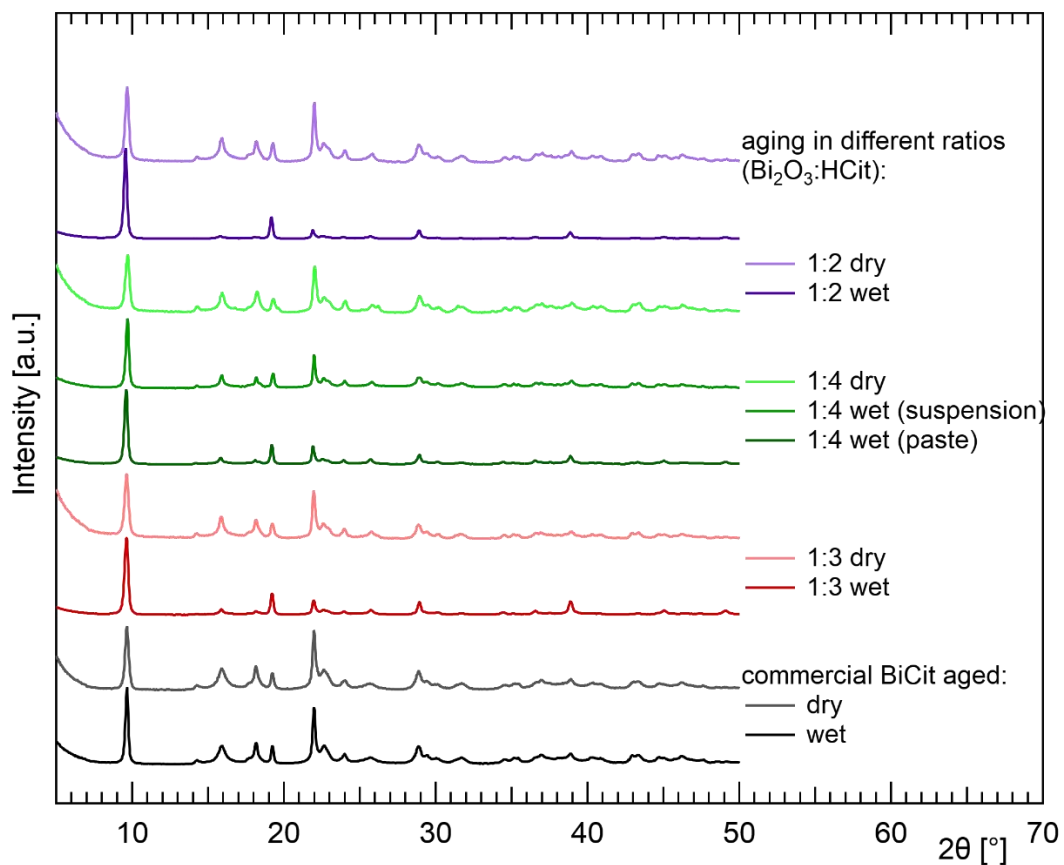


Fig. 12 PXRD of mechanochemically synthesized samples with different Bi_2O_3 to HCit ratios, measured right after synthesis. The conditions for each sample were the same, apart from no ionic salt for the 1:4 ratio and commercial BiCit. Although each sample used $75\ \mu\text{l}$ of water, the resulting consistency was not the same in all cases, presumably due to evaporation while heating implemented before each grinding, and varying ratios of precursor mixture. Therefore, the results show not only the excess of Bi_2O_3 for 3:4 and 1:1 samples, but also that the amount of water in the system, influencing the structure. For the sample with 1:2 ratio, the water possible evaporated entirely in the furnace, resulting in a poorly crystalline sample, with 2a structure visible in the pattern. Sample with more water show 2b structure.

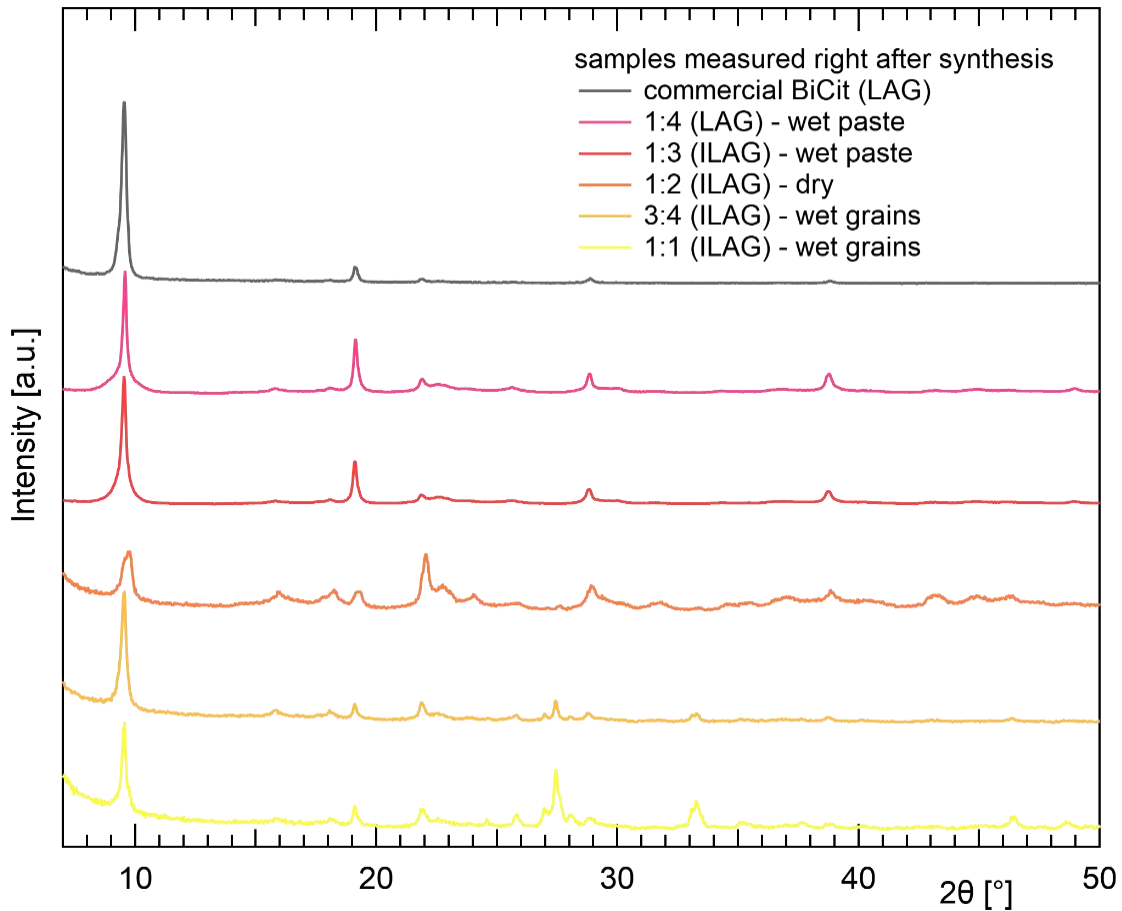


Fig. 13 PXRD patterns of commercial BiCit. **(a)**, A sample was first measured dry, then mixed with water and measured while drying, and changing from suspension to a paste. The experiment showed that the 2a structure of commercial BiCit does not change into 2b, unlike synthesized BiCit. **(b)**, Sample of commercial BiCit activated by LAG. The grinding was implemented for 300 mg of commercial BiCit, in 10 ml stainless steel jars, with two 10 mm stainless steel balls. 75 μ l of water were added to the LAG process. The jars with reaction mixture were placed in 85 $^{\circ}$ C for 30 min, before grinding for 30 min in 30 Hz frequency. The result was activating the commercial BiCit - the structure changes from 2a to 2b after the powder is mixed with water, and allowed to slowly start drying to form a paste.

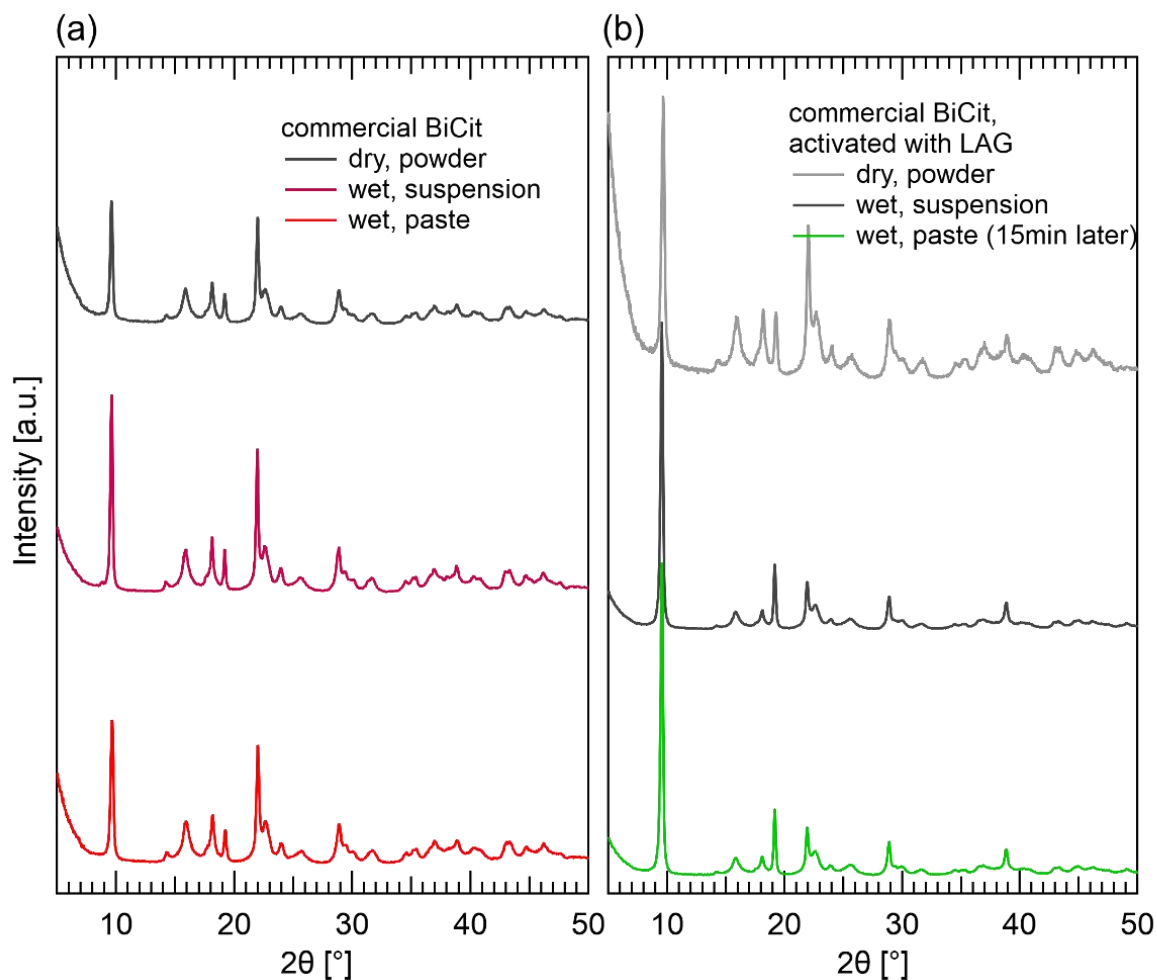
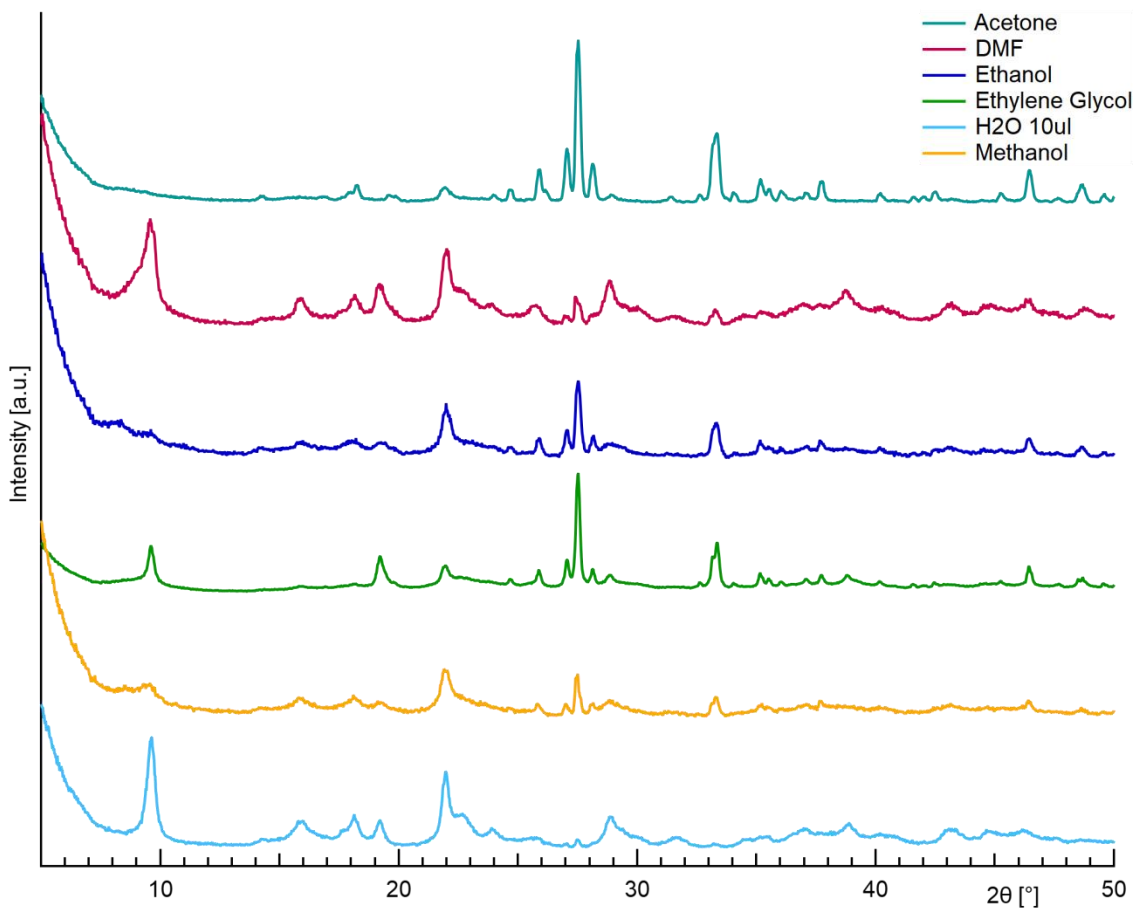


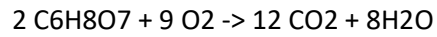
Fig. 14 PXRD patterns of commercial Bi₂O₃ ground with HCl, using alternative to water liquids. The reaction yielding BiCit takes place in DMF and Ethylene Glycol, but Ethanol and Methanol show mostly Bi₂O₃ pattern, with some traces of BiCit (22° peak). Acetone did not allow reaction to occur.



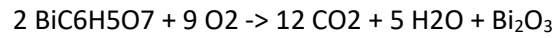
4.2. TGA

Observation of the TGA allowed to distinguish three stages of decomposition, present in BiCit samples. The stages of decomposition of bismuth citrate system, as synthesized from citric acid and bismuth(III) oxide:

- (1) Decomposition of citric acid (at 200 °C):



- (2) Decomposition of bismuth citrate (at 280-310 °C):



- (3) Not fully decomposed organic compounds (for example bismuth carbonate) decomposed further into Bi_2O_3 (at 270-410 °C)

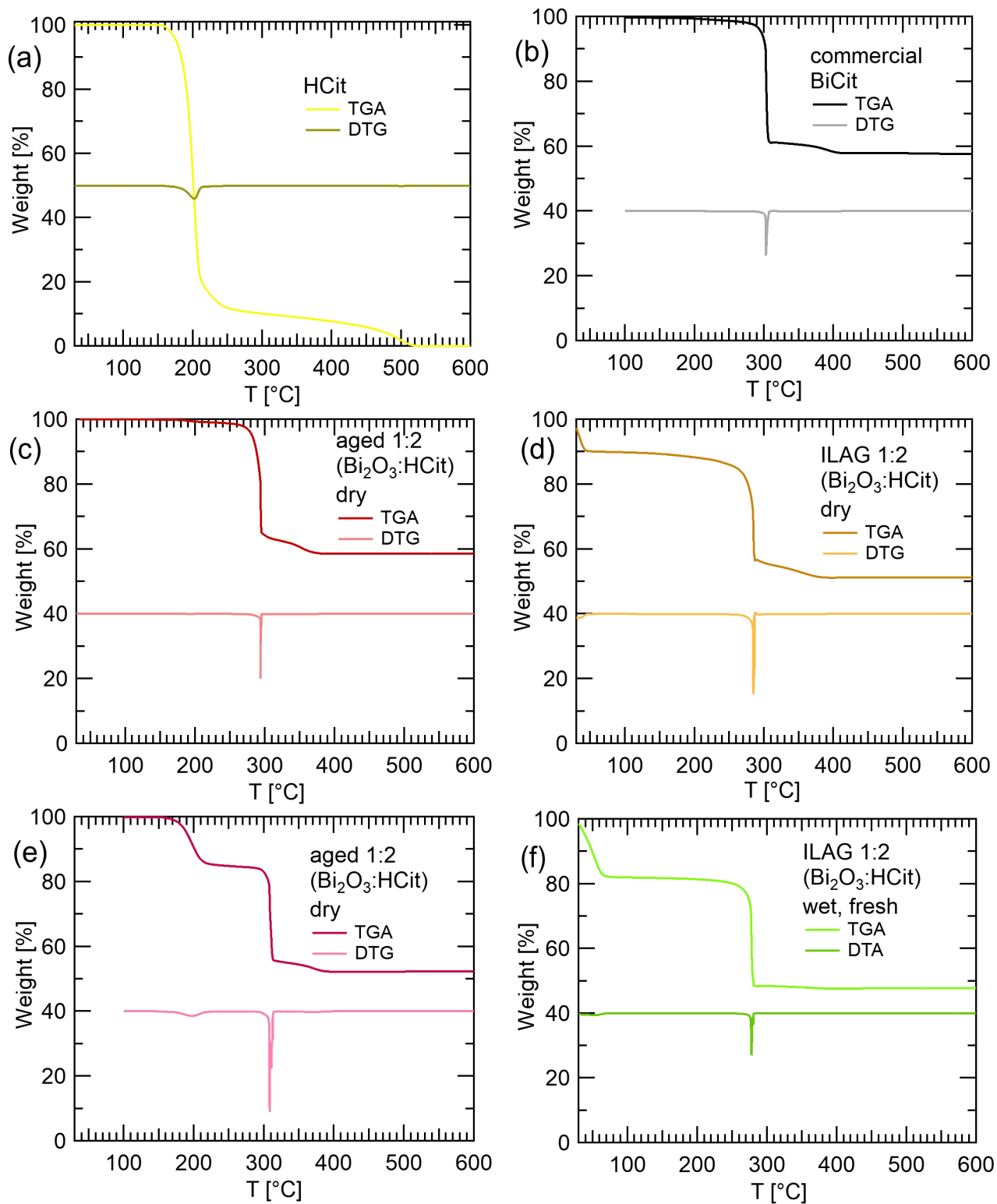


Fig. 15 TGA and DTG curves for various samples. The measurements were performed as a temperature ramp, increasing by 3-5 °C/min, from the room temperature up until 600 °C, with some, mentioned exceptions.

(a), Commercial citric acid. The measurements shows the majority of a sample decomposes at 200 °C, with 10 % of leftover decomposing over longer period of time, most probably due to not full decomposition and crystallite size.

(b), Commercial BiCit. The measurement started after the sample was exposed to 100 °C for 10 min. The TGA curve is similar to these of pure, synthesized BiCit, with no notable differences.

(c), BiCit synthesized by aging 1:2 mixture of Bi₂O₃ and HCit. The sample characterizes nearly full conversion to the BiCit. The stage attributed to decomposition of pure citric acid right below 200 °C is only slightly visible. The reaction mixture was aged in a packed crucible, allowing for a good contact in between grains and full conversion to BiCit by aging.

(d), BiCit synthesized by ILAG of 1:2 mixture of Bi₂O₃ and HCit. The sample characterizes full conversion to BiCit. The stage attributed to decomposition of pure citric acid right below 200 °C is not visible. Although the sample was visibly dry, 10 % of the initial mass was lost below 100 °C, and can be attributed to excess water content.

(e), BiCit synthesized by aging 1:2 mixture of Bi₂O₃ and HCit. The measurement started after the sample was exposed to 100 °C for 10 min.. The sample characterizes only partial conversion to the BiCit, due to the not ideal environment for aging reaction. The reaction mixture was aged on a Petri dish, which allowed grains to scatter around a bigger surface, reducing the contact in between them. The stage attributed to decomposition of pure HCit is equal to the loss of 15% of the total mass, and the measurements presents an example of not full conversion from precursor to BiCit product.

(f), BiCit synthesized by ILAG of 1:2 mixture of Bi₂O₃ and HCit. The sample characterizes full conversion to BiCit. The stage attributed to decomposition of pure citric acid right below 200 °C is not visible. The sample was measured right after synthesis, as a homogenous paste in order to measure the 2b structure. 18 % of the initial mass was water, as seen by in the loss occurring below 100 °C. Following stages match exactly those of a dry sample, revealing no information about 2b structure.

5. Tables with reaction parameters

In this section we present some of the tested reaction parameters and associated with them results and comments.

Tab. 2 Reaction parameters for chosen experiments, meant to synthesize pure BiSal₂.

BiSal ₂ synthesis																		
i.p.	sample name	substrate					liquid		ionic salt			grinding				product	comment	
		ratio		mass			H ₂ O	other	KNO ₃	NaNO ₃	NH ₄ NO ₃	time	jar	balls	heating for 30min	f		as seen with PXDR
		[Bi ₂ O ₃]	[HSal]	Total [mg]	Bi ₂ O ₃ [mg]	HSal [mg]	[μl]	[name + μl]	[%]			[min]	[ml]	no x d[mm]	[°C]	[Hz]		
1	LAG1	1	4	1018	466	552	250	0	0	0	0	30	25	2x 10	85	30	BiSal3, Bi2O3	
2	ILAG1	1	4	1018	466	552	250	0	0	1	0	30	25	2x 10	85	30	BiSal2	
3	LAG2	1	4	1018	466	552	250	0	0	0	0	30	25	2x 10	85	30	BiSal3, Bi2O3	
4	ILAG2	1	4	1018	466	552	250	0	0	1	0	30	25	2x 10	85	30	BiSal2	
5	LAG3	1	4	1018	466	552	250	0	0	0	0	30	25	2x 10		30	BiSal3, Bi2O3	ambient jar temperature (does not yield BiSal2)
6	ILAG3	1	4	1018	466	552	250	0	0	1	0	30	25	2x 10		30	BiSal3, Bi2O3	
7	LAG4	1	4	200	91,5	108,5	50	0	0	0	0	30	10	2x 7	85	30	BiSal3, Bi2O3	7mm balls struggle to convert mixture to BiSal2 fully
8	ILAG4	1	4	200	91,5	108,5	50	0	0	1	0	30	10	2x 7	85	30	BiSal2, BiSal3, Bi2O3	
9	LAG5	1	4	200	91,5	108,5	50	0	0	0	0	30	10	2x 10	85	30	BiSal3, Bi2O3	
10	ILAG5	1	4	200	91,5	108,5	50	0	0	1	0	30	10	2x 10	85	30	BiSal2	pure BiSal2
11	agingheat	1	4	5000	aging in 115°C for 3 days, high moisture												BiSal2, bismuth subsalicylate	this experimented yielded in creating mostly BiSal2 with traces of bismuth subsalicylate
12	BiSal2_large	1	4	400	183,2	216,8	100	0	0		2	45	25	2x 10	85	30	BiSal2	The best overall (larger jar)
13	BiSal2_small	2	5	200	91,6	108,4	75	0	0		2	30	10	2x 10	85	30	BiSal2	The best overall

Tab. 3 Reaction parameters for chosen experiments, meant to synthesize pure BiSal₃.

BiSal ₃ synthesis																	
l.p.	Sample name	substrate					liquid	ionic salt			grinding					product	comment
		ratio		mass			H ₂ O	KNO ₃	NaNO ₃	NH ₄ NO ₃	time	jar	balls	heating for 30min	f	as seen with PXDR	
		[Bi ₂ O ₃]	[HSal]	Total [mg]	Bi ₂ O ₃ [mg]	HSal [mg]	[μl]	[%]			[min]	[ml]	no x d[mm]	[°C]	[Hz]		
1	BiSal3_1	1	6	200	72 (oldest)	128	75			2	30	10	2x 7	85	30	BiSal2, BiSal3, Bi2O3	
2	BiSal3_2	1	6	200	72 (newer)	128	75			2	30	10	2x 7	85	30	BiSal2, BiSal3, Bi2O3	
3	BiSal3_3	1	6	200	72 (oldest)	128	75			2	30	10	2x 7		30	BiSal3, Bi2O3	
4	BiSal3_4	1	6	200	72 (newer)	128	75			2	30	10	2x 7		30	BiSal3, Bi2O3	
5	BiSal3_pub_oldBi2O3	1	6	200	73 (oldest)	128	75			2	30	10	2x 7		30	hints of BiSal3	
6	BiSal3_pub_newBi2O3	1	6	200	73 (newer)	128	75			2	30	10	2x 7		30	hints of BiSal3	
7	BiSal3_100ul	1	6	200	73	128	100			2	30	10	2x 7		30	BiSal3 with BiSal2	
8	BiSal3_0ul	1	6	200	73	128	0				30	10	2x 7		30	Bi2O3	
9	BiSal3_2x10mm	1	6	200	73	128	75			2	30	10	2x 10		30	BiSal3, Bi2O3	
10	BiSal3_1x10mm	1	6	200	73	128	75			2	30	10	1x 10		30	hints of BiSal3	
11	BiSal3_decarb	1	6	200	73	128	75			2	30	10	2x 7		30	BiSal3	"old", unreactive Bi2O3 after activation with heat used
12	BiSal3_decarb_10p	1	6	200	73	128	75			10	30	10	2x 7		30	BiSal3	unnecessary amount of salt
13	BiSal3_decarb_40min	1	6	200	73	128	75			2	40	10	2x 7		30	BiSal3	"old", unreactive Bi2O3 after activation with heat used
14	BiSal3_decarb_20min	1	6	200	73	128	75			2	20	10	2x 7		30	BiSal3, some leftover Bi2O3	"old", unreactive Bi2O3 after activation with heat used
15	BiSal3_decarb_20min_HSalDRIED	1	6	200	73	128	75			2	20	10	2x 7		30	BiSal3, some leftover Bi2O3	
16	BiSal3_UVVis_09	1	6	200	73	128	75			2	40	10	2x 7		30	BiSal3	
17	BiSal3_UVVis_10	1	6	200	73	128	75			2	40	10	2x 7		30	BiSal3	

Tab. 4 Reaction parameters for chosen experiments, meant to synthesize pure BiGall.

BiGall synthesis																		
l.p.	sample name	substrate					liquid		ionic salt			grinding					product	comment
		ratio		mass			H ₂ O	other	KNO ₃	NaNO ₃	NH ₄ NO ₃	time	jar	balls	heating for 30min	f	as seen with PXDR	
		[Bi ₂ O ₃]	[HGall]	Total [mg]	Bi ₂ O ₃ [mg]	HGall [mg]	[μl]	[name + μl]	[%]			[min]	[ml]	no x d[mm]	[°C]	[Hz]		
1	BiGall_12	1	2	200	115,59	84,4	50			2	30	10	2x 10	85	30	BiGall	best ratio	
2	BiGall_14	1	4	200	115,59	84,4	50			2	30	10	2x 10	85	30	BiGal, HGall		
3	BiGall_propanol	1	2	200	115,59	84,4		100 propanol		2	30	10	2x 10	85	30	BiGall		
4	BiGall_ethanol	1	2	200	115,59	84,4		100 ethanol		2	30	10	2x 10	85	30	BiGall (bad quality)		
5	BiGall_DMF	1	2	200	115,59	84,4		100 DMF		2	30	10	2x 10	85	30	unknown product		
6	BiGall_acetone	1	2	200	115,59	84,4		100 Acetone		2	30	10	2x 10	85	30	amorphous		
7	BiGall_water	1	2	200	115,59	84,4	100			2	30	10	2x 10	85	30	BiGall		
8	BiGall_30ul	1	2	200	115,59	84,4	30			2	30	10	2x 10	85	30	BiGall		
9	BiGall_50ul	1	2	200	115,59	84,4	50			2	30	10	2x 10	85	30	BiGall		
10	BiGall_100ul	1	2	200	115,59	84,4	100			2	30	10	2x 10	85	30	BiGall	The best amount of water	
11	BiGall_150ul	1	2	200	115,59	84,4	150			2	30	10	2x 10	85	30	BiGall		
12	BiGall_75ul_prop	1	2	200	115,59	84,4		75 propanol		2	30	10	2x 10	85	30	BiGall (bad quality)	oxide leftover very visible	
13	BiGall_100ul_prop	1	2	200	115,59	84,4		100 propanol		2	30	10	2x 10	85	30	didn't work	almost only oxide leftover visible	
14	BiGall_100ul_prop45min	1	2	200	115,59	84,4		100 propanol		2	45	10	2x 10	85	30	didn't work		
15	BiGall_75+75_prop+wat	1	2	200	115,59	84,4	75	75 propanol		2	30	10	2x 10	85	30	BiGall		
16	BiGallWat100t45	1	2	200	115,59	84,4	100			2	45	10	2x 10	85	30	BiGall	The best overall	
17	BiGall_DRY_heat	1	2	200	115,59	84,4				2	30	10	2x 10	85	30	didn't work	almost only leftover oxide visible	
18	BiGall_DRY_NOheat	1	2	200	115,59	84,4				2	30	10	2x 10		30	didn't work		
19	BiGall_LAG_heat	1	2	200	115,59	84,4	100				30	10	2x 10	85	30	BiGall		
20	BiGall_LAG_Noheat	1	2	200	115,59	84,4	100				30	10	2x 10		30	BiGall		

Tab. 5 Reaction parameters for chosen experiments, meant to synthesize pure BiCit.

BiCit synthesis																		
l.p.	sample name	substrate					liquid		ionic salt			grinding					product	comment
		ratio		mass			H ₂ O	other	KNO ₃	NaNO ₃	NH ₄ NO ₃	time	jar	balls	heating for 30min	f	as seen with PXDR	
		[Bi ₂ O ₃]	[HCit]	Total [mg]	Bi ₂ O ₃ [mg]	HCit [mg]	[μl]	[name +μl]	[%]			[min]	[ml]	no x d[mm]	[°C]	[Hz]		
1	BiCit_K	1	4	300	113,24	186,76	75		5			20	10	2x 10	85	30	BiCit	(water-filled structure as measured immediately after synthesis)
2	BiCit_NH4	1	4	300	113,24	186,76	75			5	20	10	2x 10	85	30	BiCit		
3	BiCit_30min_K	1	4	300	113,24	186,76	75		5		30	10	2x 10	85	30	BiCit		
4	BiCit_30min_NH4	1	4	300	113,24	186,76	75			5	30	10	2x 10	85	30	BiCit		
5	BiCit_noHeat_K	1	4	300	113,24	186,76	75		5		20	10	2x 10		30	BiCit, Bi2O3	reacts better with heating the jars	
6	BiCit_noHeat_NH4	1	4	300	113,24	186,76	75			5	20	10	2x 10		30	BiCit, Bi2O3		
7	BiCit_14	1	4	300	113,24	186,76	75			5	30	10	2x 10	85	30	Samples mostly yielded BiCit, but were made in order to capture 2b "wet" structure - before is was clear that it is the same chemically as 2a, just wet		
8	BiCit_16	1	6	300			75			5	30	10	2x 10	85	30			
9	BiCit_40min_75ul	1	2	300	164,4	135,6	75			5	40	10	2x 10	85	30			
10	BiCit_40min_100ul	1	2	300	164,4	135,6	100			5	40	10	2x 10	85	30			
11	BiCit_40min_75ul	1	2	300	164,4	135,6	75			5	50	10	2x 10	85	30			
12	BiCit_40min_100ul	1	2	300	164,4	135,6	100			5	50	10	2x 10	85	30			
13	BiCit_4min_10mm	1	4	300	113,24	186,76	75			5	4	10	2x 10	85	30			
14	BiCit_4min_7mm	1	4	300	113,24	186,76	75			5	4	10	2x7	85	30		2x7 mm balls can yield Bi2O3 leftover	
15	BiCit_8min_10mm	1	4	300	113,24	186,76	75			5	8	10	2x 10	85	30			
16	BiCit_8min_7mm	1	4	300	113,24	186,76	75			5	8	10	2x7	85	30		2x7 mm balls can yield Bi2O3 leftover	
17	BiCit_12min_10mm	1	4	300	113,24	186,76	75			5	12	10	2x 10	85	30			
18	BiCit_12min_7mm	1	4	300	113,24	186,76	75			5	12	10	2x7	85	30		2x7 mm balls can yield Bi2O3 leftover	
19	BiCit_16min_10mm	1	4	300	113,24	186,76	75			5	16	10	2x 10	85	30			
20	BiCit_16min_7mm	1	4	300	113,24	186,76	75			5	16	10	2x7	85	30		2x7 mm balls can yield Bi2O3 leftover	

21	BiCit_16min_Fresh	1	4	300	113,24	186,76	75				5	16	10	2x 10	85	30		
22	BiCit_16min_Fresh_HotDried	1	4	300	113,24	186,76	75				5	16	10	2x 10	85	30		
23	BiCit_DMF	1	2	300	164,4	135,6		75 DMF				30	10	2x 10	85	30	BiCit, Bi2O3	poor crystallinity
24	BiCit_Acet	1	2	300	164,4	135,6		75 Acetone				30	10	2x 10	85	30	Bi2O3	no reaction
25	BiCit_H2O_10ul	1	2	300	164,4	135,6	10					30	10	2x 10	85	30	BiCit	
26	BiCit_Methanol	1	2	300	164,4	135,6		75 Methanol				30	10	2x 10	85	30	Bi2O3	not much reaction (traces of BiCit)
27	BiCit_Ethanol	1	2	300	164,4	135,6		75 Ethanol				30	10	2x 10	85	30	Bi2O3	not much reaction (traces of BiCit)
28	BiCit_EthylGlicol	1	2	300	164,4	135,6		75 EG				30	10	2x 10	85	30	BiCit, Bi2O3	poor crystallinity
29	BiCit_1to1(1to2)	1	2	300	164,4	135,6	75					30	10	2x 10	85	30	BiCit, Bi2O3	
30	BiCit_2to3(1to3)	1	3	300	134,1	165,9	75					30	10	2x 10	85	30	BiCit, Bi2O3	
31	BiCit_2to1(1to1)	1	1	300	212,4	87,6	75					30	10	2x 10	85	30	BiCit, Bi2O3	
32	BiCit_3to2(3to4)	3	4	300	193,6	106,4	75					30	10	2x 10	85	30	BiCit, Bi2O3	
33	BiCit_commercial_LAG			300			75					30	10	2x 10	85	30		Discovering the possibility to "activate" commercial BiCit by grinding it, to obtain the "wet" structure
34	BiCit_1to2(1to4)	1	4	300	113,24	186,76	75					30	10	2x 10	85	30	BiCit	Full conversion to BiCit, no Bi2O3 traces and no use of ionic salt