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„Physicochemical characterization of lamellar precipitated calcium carbonate (PCC)“

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Declaration

I hereby declare that this thesis contains no material, which has been submitted or accepted for an award of any other degree or diploma in any university or institution. To the best of my knowledge and belief, this thesis contains no material previously published by any other person except where acknowledgment has been made.

Vienna, November 2019

Dominic D. Öhre

Abstract

Lamellar precipitated calcium carbonate (PCC) is a material, which has been produced via a method as described in a doctoral research by Sousa (2016) and could find potential application in paper manufacturing.

Different physicochemical analyses have been used and show, lamellar PCC is not a carbonate but a citrate. However, it is unknown in database such as Cambridge database or ICSD but show similarities with different types of citrates. The substance contains one phase and forms planar and acicular crystals, which could be visualized in SEM imaging.

Lamellar PCC disintegrates while heating to a temperature of 1100°C through steps and releases mainly CO_2, CO and H_2O. Intermediates consist of neyererit, disodium citrate and portlandite around the end temperature of 1100°C only calcium oxide can be found. The substance shows also a complete solubility in water and has, when fully dissolved in water, a pH of 5.5.

Through FTIR the sample could be identified as calcium sodium citrate ($C_6H_5CaNaO_7$), of which the chemical composition could be confirmed via EDX analysis.

A structural model of calcium sodium citrate is yet not known, a structural determination has been started, but no structure could be found by now.

Zusammenfassung

Lamellar precipitated calcium carbonate (PCC) ist ein Material, das analog einer Doktorarbeit von Sousa (2016) hergestellt wurde und eine potentielle Anwendung in der Papierindustrie findet.
Verschiedene chemische und physikalische Untersuchungen zeigten, dass es sich nicht um ein PCC handelt, sondern um ein Citrat, das jedoch weder in der Cambridge Database noch ICSD bekannt ist. Pulverspektrum weisen jedoch Ähnlichkeiten mit Citraten auf. Die Substanz ist einphasig und bildet stäbchen- bis plättchenförmige Kristalle, die im SEM Bild aufgenommen wurden.
Lamellar PCC zerfällt beim Erhitzen auf 1100°C in mehreren Schritten und gibt hauptsächlich CO_2, CO und H_2O ab. Zwischenprodukte des Zerfalls umfassen Neyererit, Portlandit und Dinatriumcarbonat. Bei 1100°C bleibt hauptsächlich Calciumoxid übrig.
Des Weiteren ist die Probe vollständig wasserlöslich und hat ein pH-Wert von rund 5.5, wenn vollständig gelöst.
Mit Hilfe von einer FTIR Analyse konnte die Substanz auf Calciumnatriumcitrat ($C_6H_5CaNaO_7$) identifiziert werden und mit Hilfe einer EDX Messung konnte diese Zusammensetzung bestätigt werden.

Eine Kristallstruktur von Calciumnatiumcitrat ($C_6H_5CaNaO_7$) ist bisher noch unbekannt, ein Strukturbestimmung der Probe wurde begonnen, jedoch wurde noch keine passende Struktur gefunden.

Index

1. Introduction

This research study deals with the formation respectively the precipitation of calcium carbonate or as described by Omya International AG „lamellar Precipitated Calcium Carbonate (lamellar PCC)“ as well as its structural and physiochemical characterization, based on sample material supplied by Omya International AG. Sample materials of lamellar PCC will be analyzed with powder X-ray diffraction (PXRD), thermal analysis (TA), chemical analysis, electron microscopic imaging (SEM) and spectroscopic methods at the Department of Mineralogy and Crystallography at University of Vienna.

Precipitated calcium carbonate (PCC) has been known for many years and its structure and properties are well studied. Nonetheless it has been still investigated further to improve properties of PCC and to simplify production. PCC is a purer than grained calcium carbonate. Its formula is the same as calcium carbonate → $CaCO_3$. The name mainly comes from the industrial use and the process of producing, as it precipitates from an aqueous solution.

Precipitated calcium carbonate has a significant role in industrial operation as well as natural occurring process. It can be found in many applications, such as in paper, rubber or as pigment and is needed in a high amount as mentioned by Söhnel and Mullin (1982).

Trubey (patent application US2962350A, 1957) described a process of producing pure PCC from raw materials containing calcium and magnesium via slurring and introducing with carbon dioxide. In literature there are various ways described to obtain PCC and there is ongoing research to find best results for specific needs of the final product.

Newer methods are described for instance by Maurer et al. (patent application EP20130181073 2013) producing PCC with a higher aragonite crystal polymorph weight percentage. Aragonite is from importance as it can be used as inorganic filler or paper coating and because of its needle like shape it offers enhanced paper bulk and opacity.

2. Literature review

2.1. Synthesis of precipitated calcium carbonate

Calcium carbonate can be synthesized by many methods as found in abundant literature about this topic. As described in almost all references Precipitated Calcium Carbonate (PCC) is made by direct carbonation of hydrated lime due to its low cost and the abundance of the raw materials:

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3$

The process involves following steps (Jimoh et al., 2017), Mining calcium carbonate rock with a high purity and crushing the rocks into small stones or powder, depending on the particle size needed for processing. Impurities are separated from the powder/ small rocks. Through heating the pure crushed rocks in a kiln to about 1000° C, the carbonate transforms into lime (CaO) and carbon dioxide (CO_2). The CO_2 can be captured, to reuse for further processes:

$CaCO_3 + \Delta \rightarrow CaO + CO_2\uparrow$

In the next step the lime will then be added to water to form calcium hydroxide/hydrated lime/slake ($Ca(OH)_2$):

$CaO + H_2O \rightarrow Ca(OH)_2$

Additionally, remaining impurities are separated from the hydrated lime furthermore and the captured carbon dioxide is then combined with the hydrated lime, in which calcium carbonate can be reformed. As the calcium carbonate is insoluble in water, it precipitates out. If there still impurities present, they can be separated again. Dependent on usage the PCC slurry can be used as is or dewatered, dried and milled

Often PCC is coated with different acids to increase the dispersibility in polymer or solvent as well as its compatibility with the polymer or solvent.

2.2. Relationship between morphology and precipitation condition

The morphology and size of the particles are classified as rhombic calcite, needle-like aragonite and spherical vaterite. The different space groups and lattice constants are $R\bar{3}c$, a = 4.990, c = 17.061 Å $\alpha = 90°$ $\gamma = 120°$; Z = 6 for calcite, Pmcn, a = 4.9598 , b = 7.9641 , and c = 5.7379 [Å] and $\alpha = 90°$ for aragonite and $P6_3/mmc$, a = 4.13, c = 8.48 [Å] $\alpha = 90°$ $\gamma = 120°$; Z = 6 for vaterite (de Leeuw and Parker, 1998). These types are dependent on the precipitation conditions and the dispersion of CO_2. There has been a considerably amount on research about the relationship of precipitation condition and the morphology of the particles, as described by Xiang et al. 2002. The usage of different additives to change the crystallization of these particles has been tested and as results show, different additives show different behaviors in the precipitation process of calcium carbonate.

Taft (1967) states that there is a necessity of a critical magnesium : calcium concentration ratio to prevent transformation of aragonite into calcite. Kawano and Tokonami (2014) described the inhibition of precipitation of calcium carbonate with the use of organic acids, such as citric acid, malic acid and acetic acid, in a solution of Mg^{2+} ions and therefore minimizing the formation of aragonite. Best results have been accomplished with citric acid and decrease from malic to acidic acid

2.3. Structural and physiochemical characterization

PCC manly consists of calcium carbonate and primarily in its structural composition of calcite. Calcite has a distinctive PXRD pattern (Fig. 1), which can be easily identified and has been known for years.

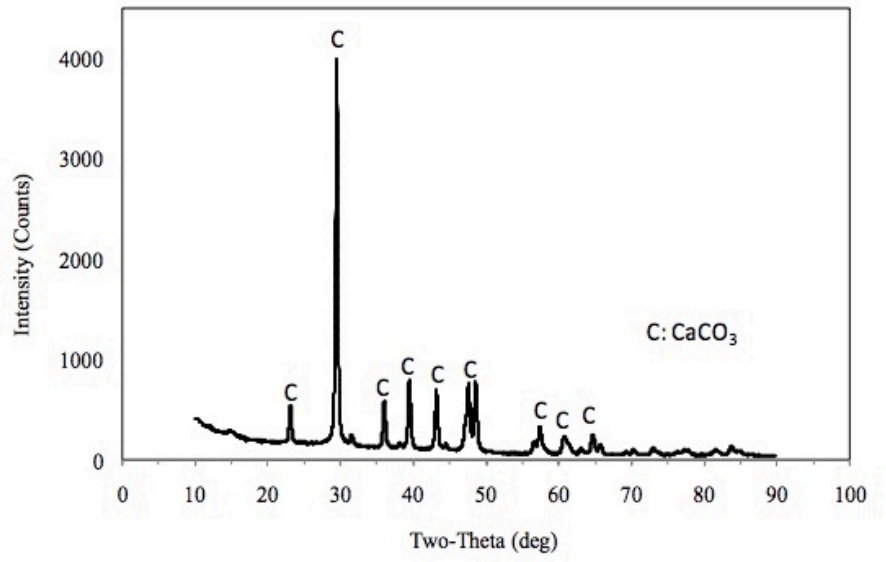

Fig. 1) PXRD pattern of PCC (Erdogan and Eken, 2015)

X-ray powder diffraction provides an easy way to distinguish between the polymorphs of calcium carbonate, as they have their highest intensity peaks at different peak positions and the overall shape of the pattern differs, as shown by Ni and Ratner in 2008.

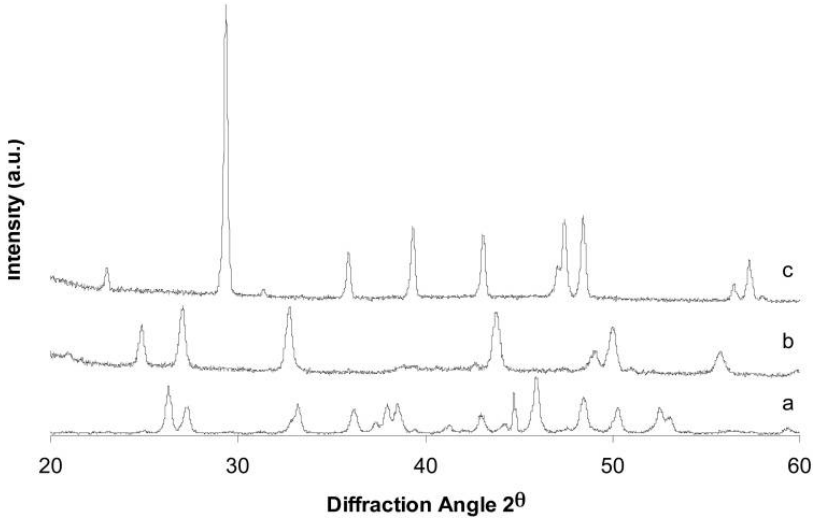

Fig. 2) X-ray patterns of calcium carbonate polymorphs, a) aragonite, b) vaterite, c) calcite, Ni and Ratner, 2008

Ni and Ratner also showed the different spectra in Fourier Transformation Infrared Spectroscopy (FTIR), where a shift of the absorption can be observed. From calcite to aragonite there is a shift towards higher wavenumbers (Fig. 3)

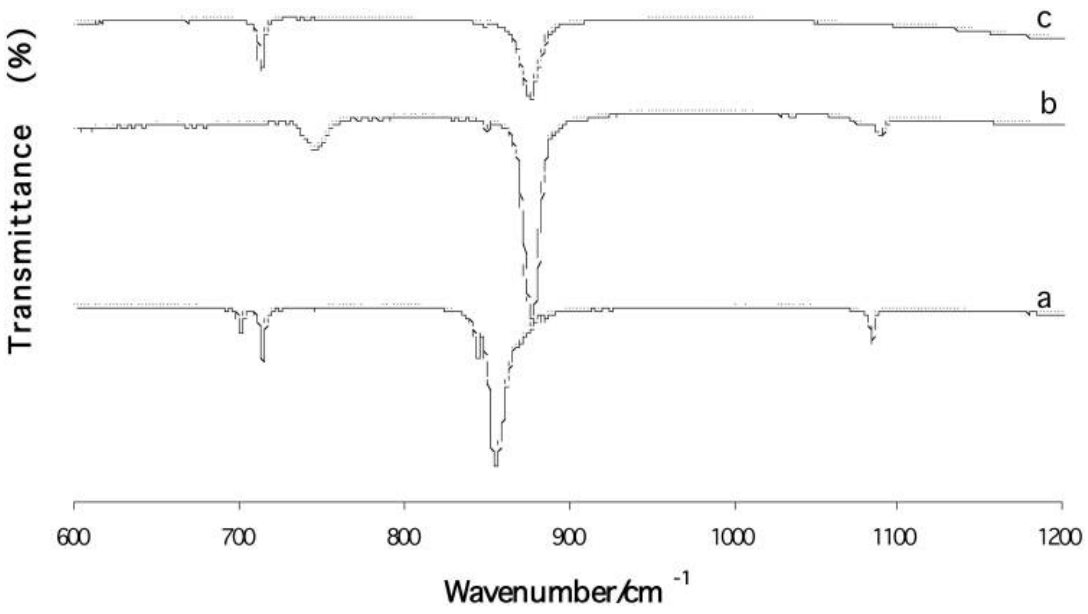

Fig. 3) FTIR spectra of calcium carbonate polymorphs, a) aragonite, b) vaterite, c) calcite, Ni and Ratner (2008)

PCC can be produced in different shape and particle sizes dependent on different conditions during formation or through usage of additives. All these also vary in physical properties, which can be used for different applications. In example prismatic shapes are designed to give high brightness and whiteness (Wise, 1997), as scalenohedral shapes are designed to supply increased paper opacity and brightness in uncoated fine papers (Klungness et al., 1998). The industry is especially interested in a variety of new properties and research is pushed ahead. With application of secondary electron microscopy (SEM) these shapes can be visualized. Examples are shown in Fig. 4 and Fig. 5.

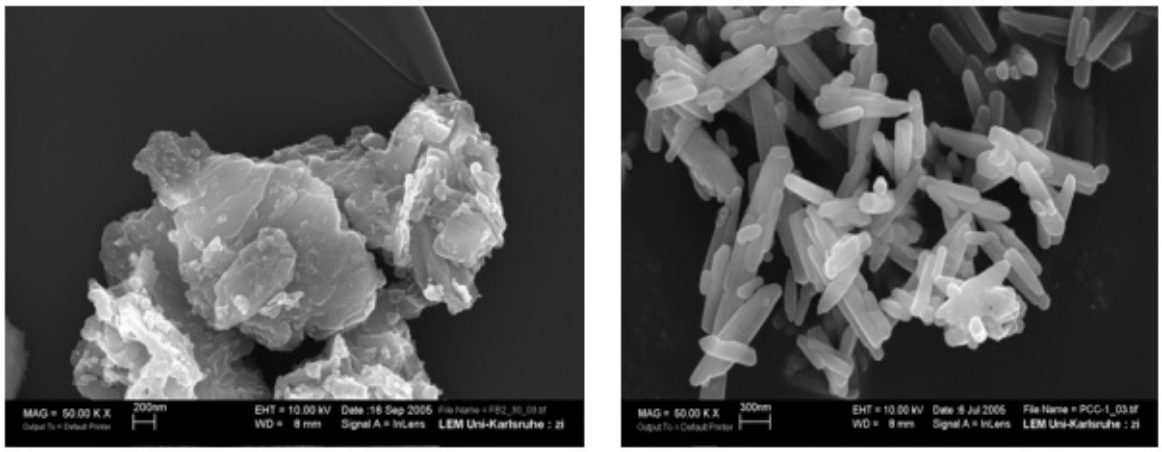

Fig. 4) SEM images of PCC aggregates in plate and prismatic shape, Katayoon (2007)

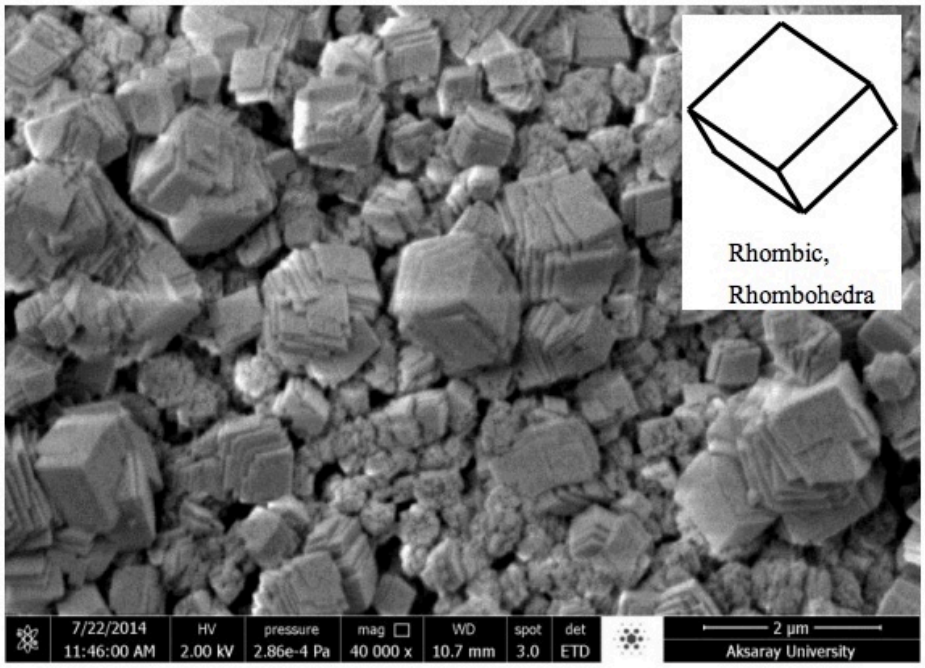

Fig. 5) SEM image of PCC in rhombic shape, Erdogan and Eken (2017)

PCC contains mostly calcium carbonate and therefore behaves like it. However, behavior parameters can be changed with certain additives. The thermal decomposition of calcium carbonate polymorphs is well studied, and it is known with increasing temperature it will decompose into calcium oxide, also known as quicklime, and carbon dioxide (Hyatt et al. 1958):

$CaCO_3 \rightarrow CaO + CO_2 \uparrow$

At around 900°C calcium carbonate has entirely transformed into quicklime, whereas carbon dioxide escaped as gas.

In a Publication by George T. Faust (1950) the thermal behavior of calcite and aragonite has been studied by thermogravimetric analysis and differential thermal analysis (DTA). Calcite and aragonite thermally behave almost identical and decompose at 615°C. Fig. 6 shows a TGA of calcium carbonate, in which different heating rates have been used, 5°C/min, 10°C/min and 20°C/min. The different heating values do not really change the decomposition of calcium carbonate, except a slight change of the final temperature at which the reaction is complete. Higher rates move the end temperature more towards higher temperatures. In Fig. 7) the TG and DTA curve of calcium carbonate is shown.

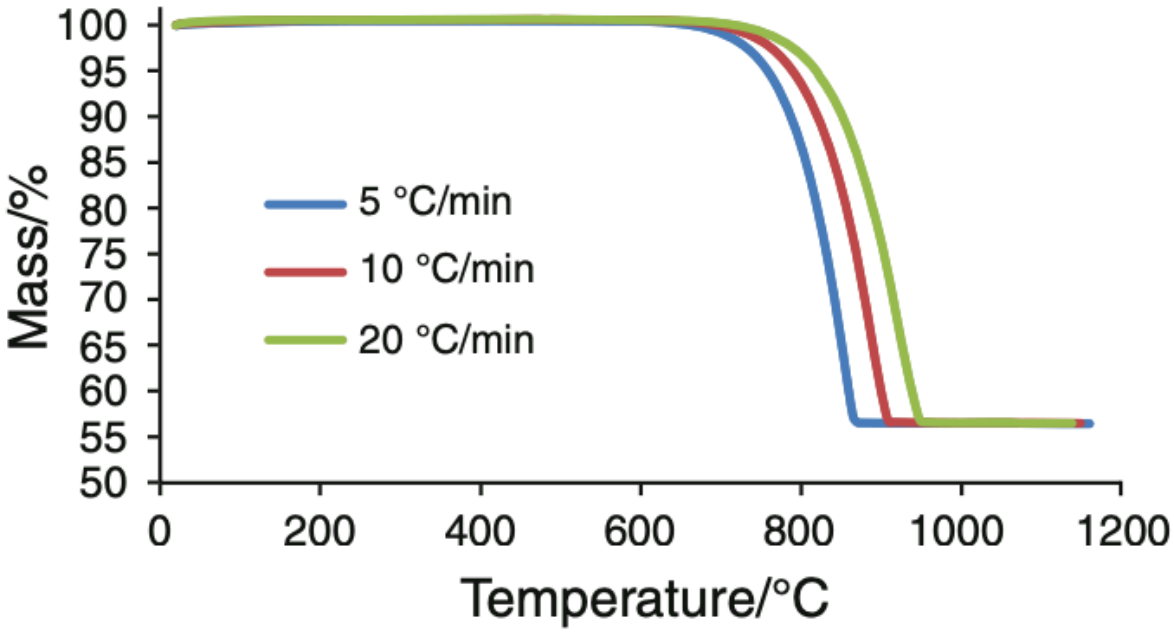

Fig. 6) Thermogravimetric analysis of calcium carbonate, Galan et al. (2013)

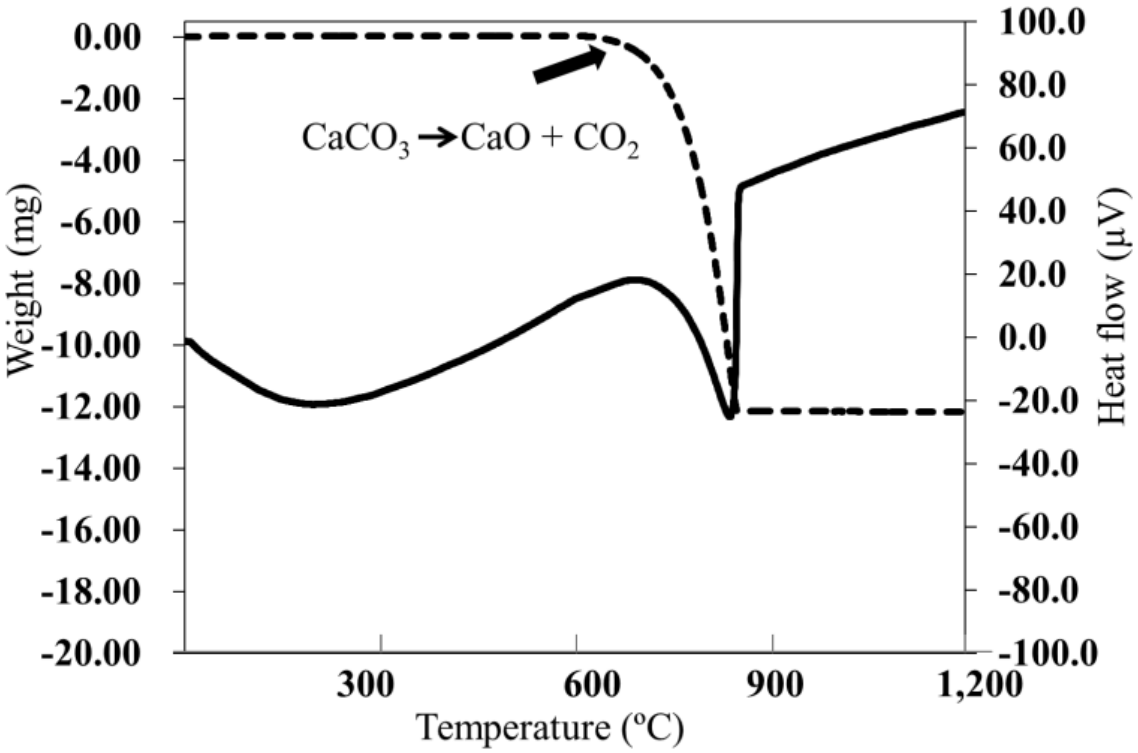

Fig. 7) TG-DTA curve for calcium carbonate, Ymaguchi et al. (2015)

In a publication by Li et al. (2013) decomposition characteristics of calcium carbonate containing organic acids, such as citric acid, oxalic acid and tartaric acid, have been investigated. The decomposition process of the mixtures of calcium carbonate and organic acids can be divided into three parts, dehydration of organic salts and decomposition of organic acids, decomposition of organic salts and combustion of products and decomposition of $CaCO_3$. The decomposition temperature decreases with incorporation of organic acids. Heat absorption due to the decomposition of the mixtures containing organic acids. TGA and Differential thermogravimetry (DTG) has been used and shows the different mixtures decompositions (Fig. 8).

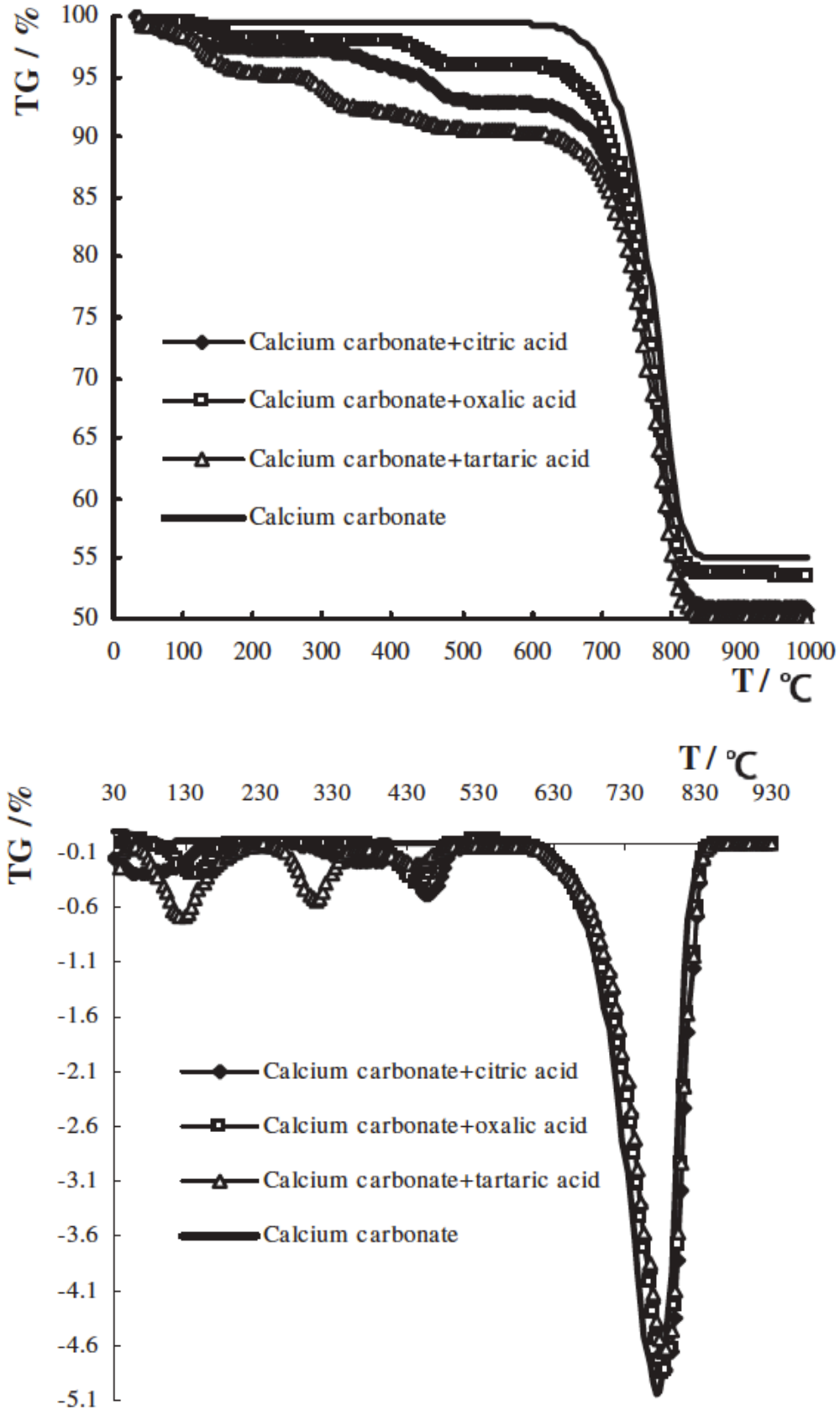

Fig. 8) TGA and DTG of calcium carbonate incorporating different organic acids, Li et al. (2013)

2.4. Application of additives

Westin and Rasmuson (2004) described additives like citric acid (CIT), diethylenetriaminepentaacetic acid (DTPA) and ethylenediaminetetraacetic acid (EDTA) influence the induction time of calcium carbonate nucleation. This results in smaller crystals sizes and hence a finer powder. Furthermore, the purity of PCC can be increased without additional treatments to get rid of impurities.

Mantilaka et al. (2014) also used the additives CIT, DTPA and EDTA to prepare PCC. In addition, sucrose has also been used. Each additive has its own effect on the created PCC and creates different shapes or sizes of the crystals, which makes all additives usable for production of PCC. However, a specific additive has to be selected to get the desired property. In comparison best results are made with sucrose which comes closest to a saturated solution of $Ca(OH)_2$ as seen in a PXRD pattern Fig. 9 and in a FTIR spectrum of each product in Fig. 10.

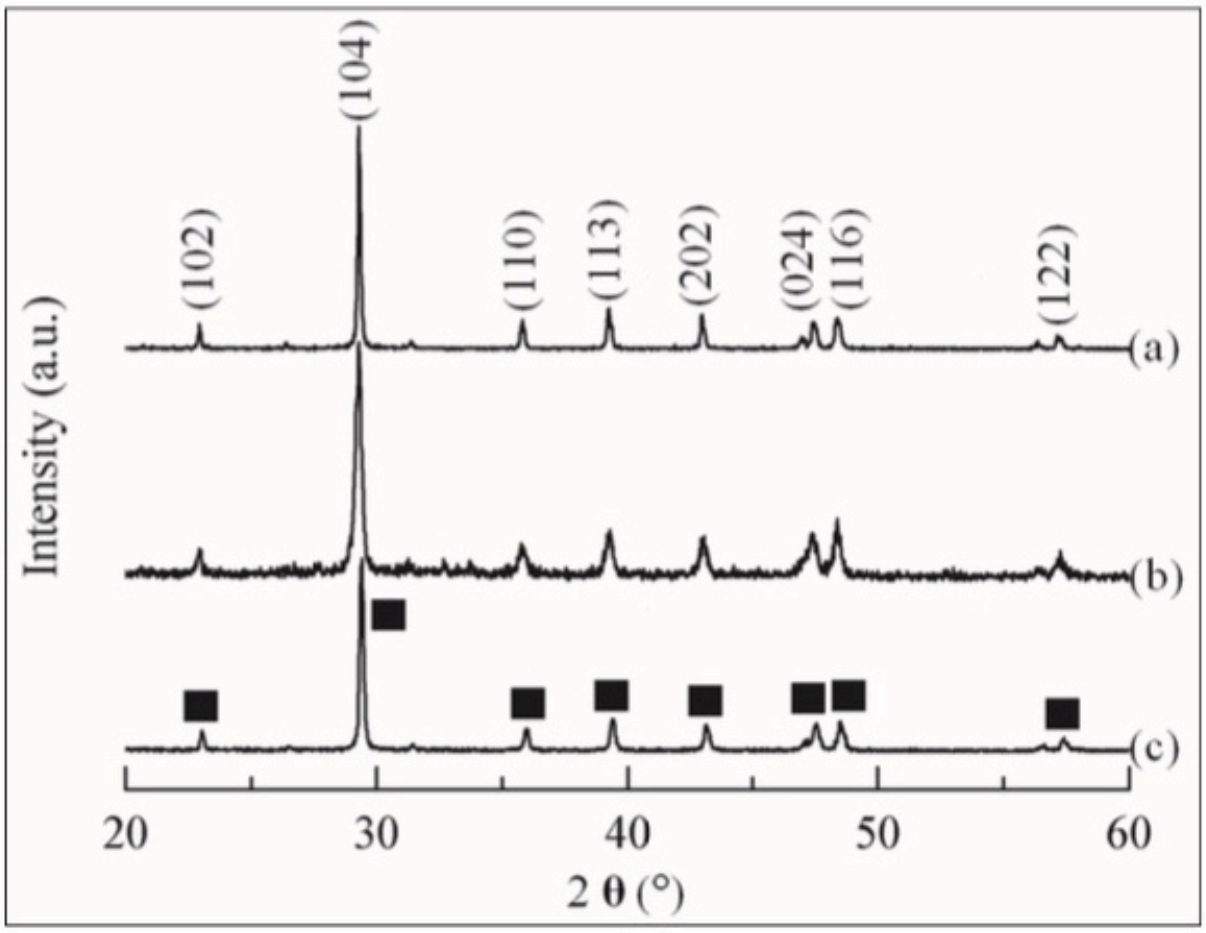

Fig. 9) PXRD patterns of PCC products prepared from a) saturated solution of $Ca(OH)_2$ b) calcium citrate complex and c) calcium sucrate, Mantilaka et al. (2014)

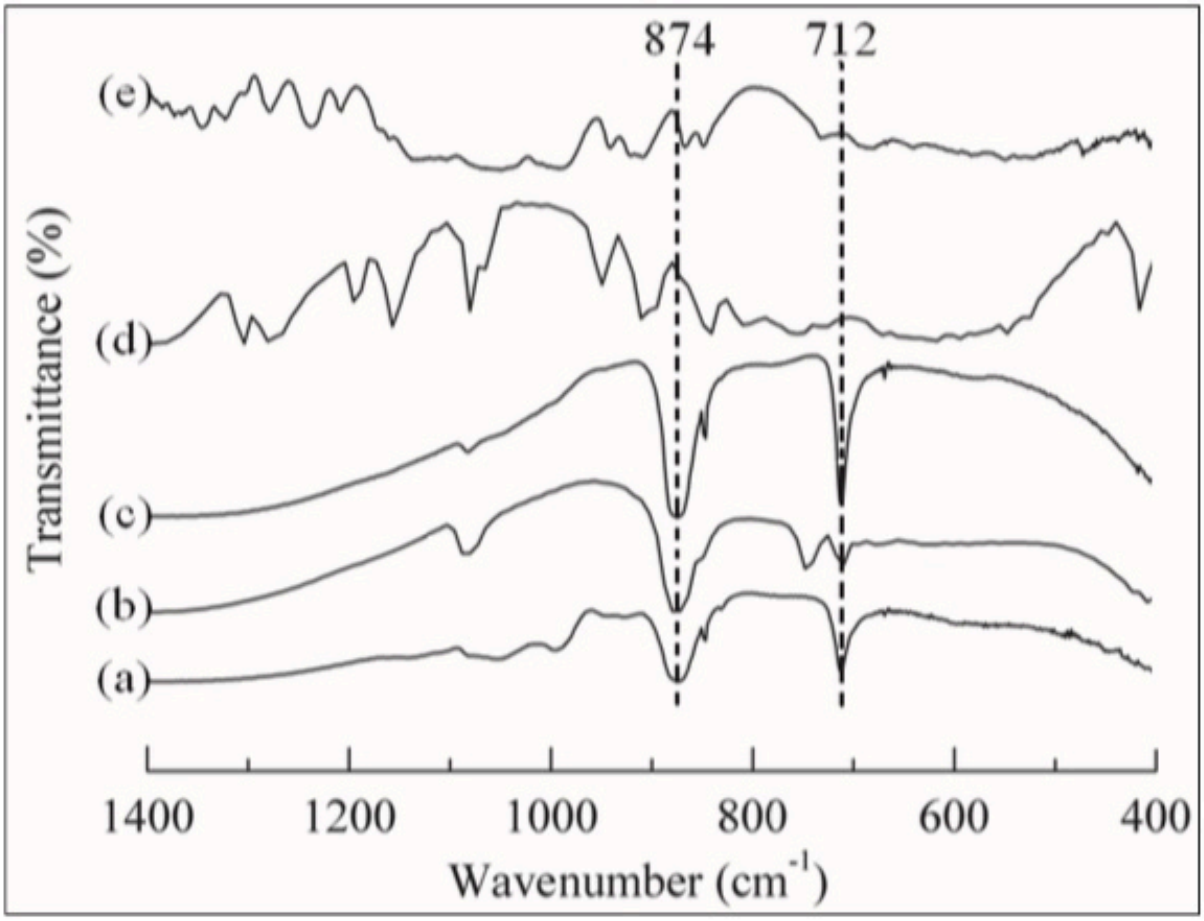

Fig. 10) FTIR spectra of PCC prepared from a) saturated solution of $Ca(OH)_2$ b) calcium citrate complex c) calcium sucrate d) trisodium citrate and e) sucrose, (Mantilaka et al. 2014)

In an article by Ghiasi and Malekzadeh (2012), the synthesis of calcium carbonate via the citrate sol-gel method (Khazaei et al. in 2010) was described. To prepare calcium carbonate nanoparticles a solution of calcium nitrate is added to a solution of citric acid. The solution is the evaporated at 60°C overnight. In the next step the obtained materials are subsequently dried at 80, 150 and 200°C. The samples are the completely powdered on each drying. Then the materials are calcined at 600°C for 5h with a heating rate of 10 K/min from room temperature. By powdering and calcining the materials further by a heating rate of 10 K/min to a temperature of 900°C for another 5 h from room temperature calcium oxide can be obtained (Singh and Singh in 2007). Calcium hydroxide is the prepared by sonication or stirring of calcium oxide in water for 20 min at room temperature (Galvan-Ruiz et al. 2009).

FTIR and PXRD of the fresh samples 1- 5 (table 1) as after calcining at 600°C (Fig. 11) and 900°C (Fig. 12) were taken. In the calcined FTIR spectra it can be observed the presence of a carbonate phase similar to calcium carbonate reported in literature. This phase shows the main bands of calcium carbonate at 715, 880, 1490, 1804, 2530, 2900 and 2998 cm^{-1} (Dong and Mater in 2009). PXRD patterns of the samples 1-5 match those of rhombohedral calcite phase with lattice parameters that are presented is table and are detected as the only phase, formed on calcining 600°C. The (104) peak can be observed as strongest, which suggest that calcium carbonate nanoparticles grow mainly parallel the (104) face (Karar et al., 2015).

Table 1 Experimental conditions for preparation of $CaCO_3$, CaO and $Ca(OH)_2$, (M. Ghiasi and A. Malekzadeh, 2012)

Sample #	c (mol.dm^{-3}) of citric acid	θ (°C) of calcination	t (min) of sonication	Sample	Polymorphism
1	0	600	-	$CaCO_3$	Calcite
2	2	600	-	$CaCO_3$	Calcite
3	5	600	-	$CaCO_3$	Calcite
4	10	600	-	$CaCO_3$	Calcite
5	10	600	20	$CaCO_3$	Calcite
6	0	900	-	CaO	Lime
7	2	900	-	CaO	Lime
8	5	900	-	CaO	Lime
9	10	900	-	CaO	Lime
10[b]	10	900	20	CaO	Lime
11[c]	10	900	20	$Ca(OH)_2$	Portlandite
12[d]	0.2	900	-	$Ca(OH)_2$	Portlandite

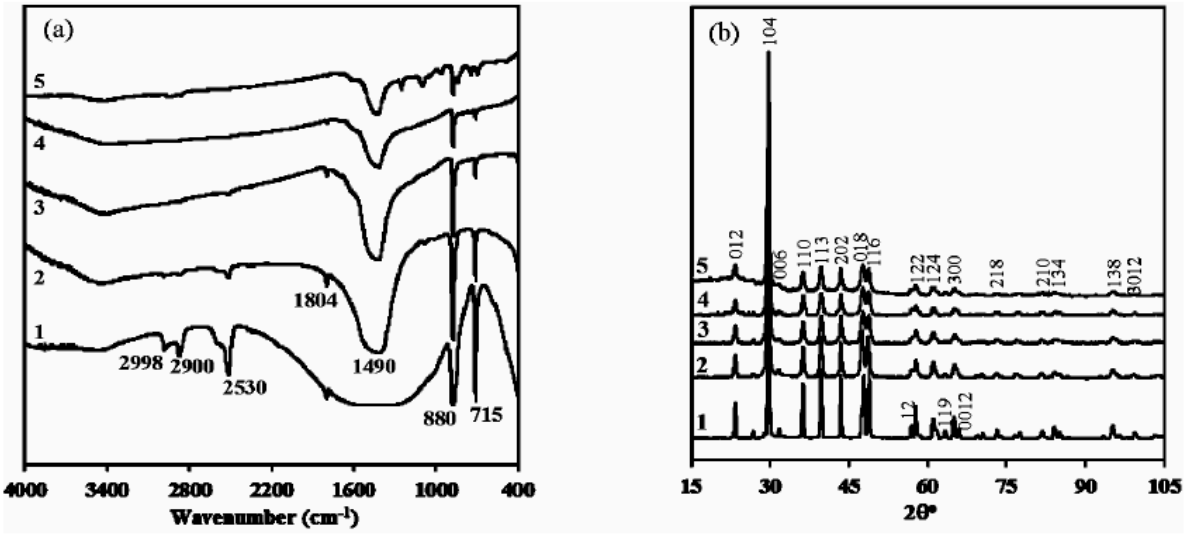

Fig. 11 a) FTIR spectra and b) PXRD pattern of samples after calcining at 600°C, Ghiasi and Malekzadeh (2012)

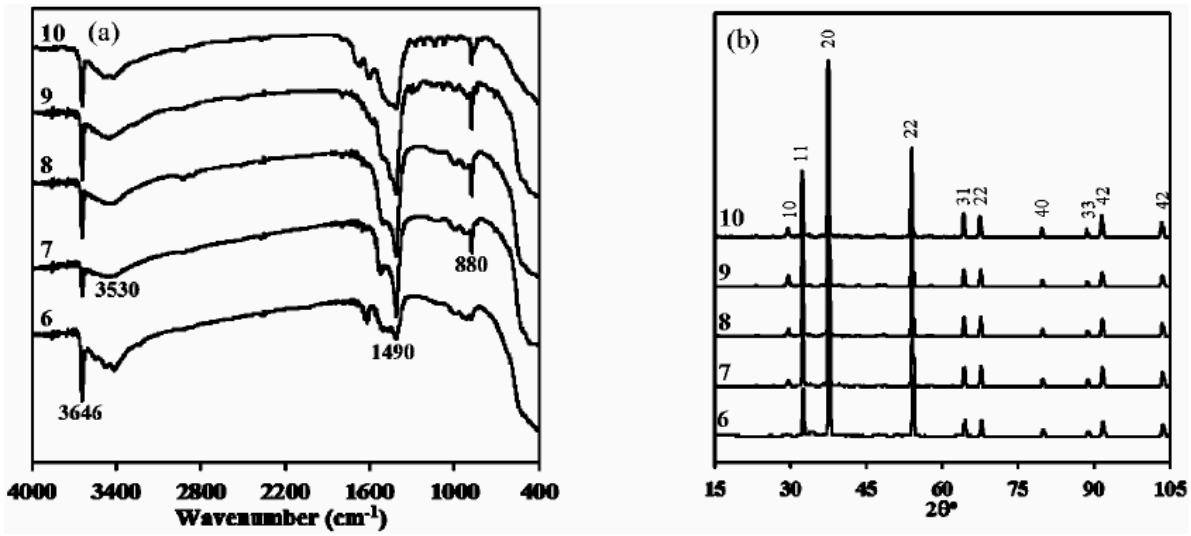

Fig. 12 a) FTIR spectra and b) PXRD pattern of samples after calcining at 900°C, Ghiasi and Malekzadeh (2012)

Table 2 Crystallographic parameters of synthesized samples (M. Ghiasi and A. Malekzadeh, 2012)

Sample #	Compo-sition	Crystal system	*a* (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)	Density (g/cm^3)	Cell volume (Å^3)
1–5	$CaCO_3$	Rhombohedral	4.9896	4.9896	17.0610	90	90	120	2.71	367.85
6–10	CaO	Cubic	4.8105	4.8105	4.8105	90	90	90	3.35	111.32
11,12	$Ca(OH)_2$	Hexagonal	3.5899	3.5899	4.9160	90	90	120	2.24	54.87

Using Scherrer and Williamson-Hall equations the average crystallite size could be estimated by PXRD data and is shown in table (Khazaei et al., 2010). With increasing concentration of citric acid results showed that the crystallite size of calcium carbonate decreased about 50%. The best molar ratio of citric acid to nitrate ions is 2.5. The size of $CaCO_3$ nanoparticles were under 25 nm.

Table 3 Crystallite size (nm) of synthesized samples. Calculations were done using Scherrer (Sa) and Williamson–Hall (WHb) equationsc. (M. Ghiasi and A. Malekzadeh, 2012)

Sample #	Nanoparticle	$S^{a,d}$	$S^{a,e}$	$S^{a,f}$	$WH^{b,d}$	$WH^{b,e}$	$WH^{b,f}$
1	$CaCO_3$	44	43	47	52	54	56
2	$CaCO_3$	29	25	26	32	30	31
3	$CaCO_3$	21	19	19	25	24	26
4	$CaCO_3$	20	19	19	25	24	25
5	$CaCO_3$	24	18	19	24	24	28
6	CaO	47	43	47	54	50	73
7	CaO	47	42	46	47	43	50
8	CaO	44	37	43	43	42	49
9	CaO	42	32	39	41	39	46
10	CaO	43	31	37	40	39	46
11	$Ca(OH)_2$	33	27	33	46	41	47

2.5. Preparation of metal citrates from metal carbonates and citric acid

Another usage for PCC is the preparation of calcium citrate from PCC and citric acid. Hereby PCC is dissolved in citric acid and the resulting compound is then dried. Calcium citrate is a commonly used food additive for prophylaxis of osteoporosis. This method can be used for a variety of metal carbonates.

Herdtweck et al. (2011) described in a study the synthesis of tri-calcium di-citrate tetra-hydrate ($[Ca_3(C_6H_5O_7)_2(H_2O)_2] * 2H_2O$) by dissolving $CaCO_3$, $Ca(NO_3)_2 * 4H_2O$ and anhydrous citric acid in DI water. Afterwards the solution was placed in a Teflon tube and sealed in a pressure vessel. Followed by heating to 160°C and kept at this temperature for 72h. After cooling to room temperature colorless needle-shaped crystals were formed.

In a publication by Cigler and Kaduk (2018) new compounds could be created. The formula of these compounds is described with $LiMHC_6H_5O_7$ (M = Li, Na, K, Rb) and their structure has been analyzed and refined. All compounds crystalize in triclinic space group $P\overline{1}$, and are nearly isostructural. The structures are lamellar, with the ab plane.

Kaduk (2018) also described the different structures of calcium citrate hexahydrate, a new polymorph of calcium citrate tetrahydrate and anhydrous calcium citrate. The structures are illustrated in Fig. 13. Different sorts of chelation can be observed in these compounds, which endorses the normally good chelating agent property of citrate anions. In a different publication by Rammohan and Kaduk (2018) 16 new alkali metal citrates could also be determined. Via density functional techniques the citrate structures were optimized.

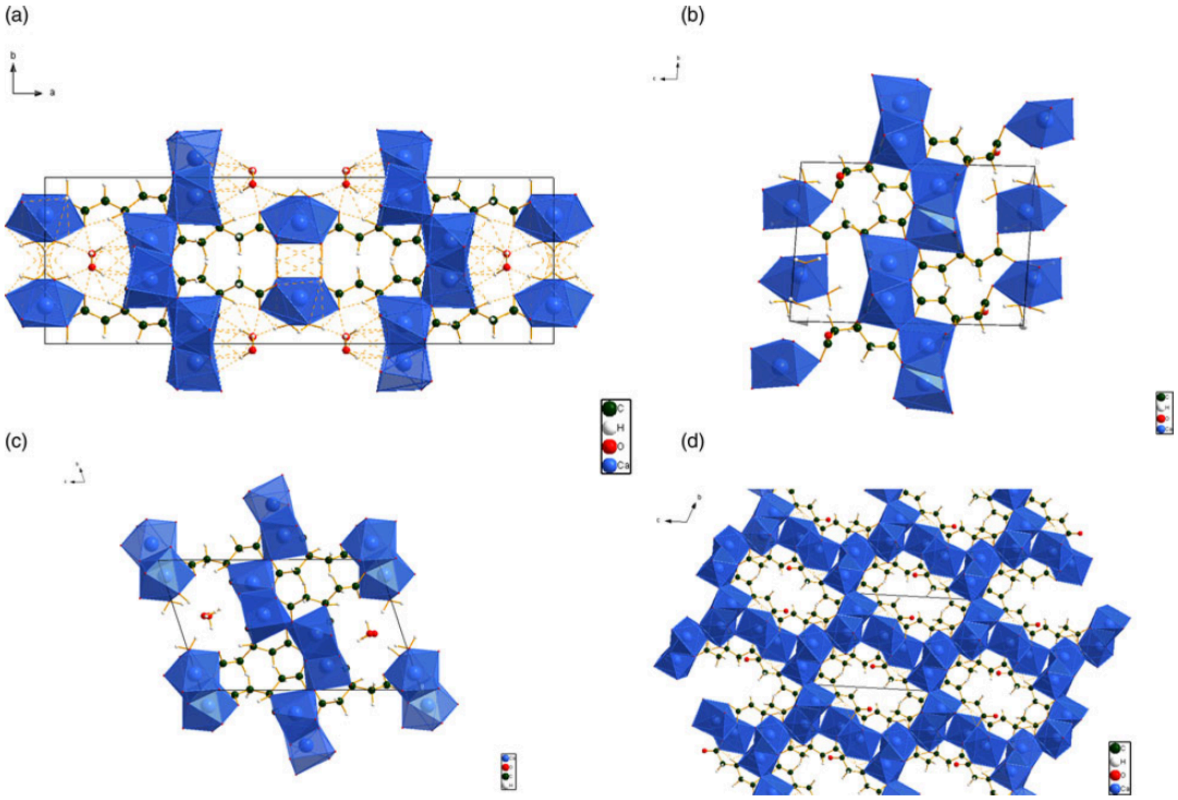

Fig. 13 a) The DFT-optimized crystal structure of calcium citrate hexahydrate, viewed down the c-axis, b) The DFT-optimized crystal structure of the new polymorph of calcium citrate tetrahydrate, viewed down the a-axis, c) The DFT-optimized crystal structure of the ISEQIH polymorph of calcium citrate tetrahydrate, viewed down the a-axis, d) The DFT-optimized crystal structure of anhydrous calcium citrate, viewed down the a-axis (Kaduk 2018).

2.6. Application

PCC has an industrial importance for many applications in example as filler in composite materials such as plastics, textiles, rubbers, paints, pigments and paper. (Xiang et al., 2002).
L. Domka (1993) mentioned in his research the usage of surface coating of PCC nanoparticles, which allow a higher surface hydrophilicity and improved monodisperse character. Many physical and chemical properties can be improved, which allow new application fields as for example improve thermal stability, which lets PCC based paint be used in higher temperature environments.

3. Sample material

Lamellar PCC consist of a fine white powder, which was produced with a method described by Sousa (2016). The procedure consists of the following steps:

Step 1 Preparation of 1 M Citrate Buffer and pH 4.5

1. To prepare 1 M citrate buffer of pH 4.5, weigh 210 g of Citric Acid monohydrate ($C_6H_8O_7 \cdot H_2O$).
2. Add 750 mL of distilled water. Stir magnetically until dissolved completely.
3. Adjust the pH of the mixture to pH 4.3 with sodium hydroxide (NaOH), about 50 to 60 g.
4. Add the solution to a 1000 mL dilution flask and top it with water. Measure pH, if not set to 4.5, adjust again with NaOH.

Step 2 White PCC Assay

1. Place about 2 g of pre-dried industrial PCC in a 400 ml beaker. Add 50 mL of ultrapure water.
2. Place in vigorous magnetic stirring to form a homogeneous suspension, with gradual heating up to 50 ° C.
3. Add the 1 M citrate buffer solution at pH 4.5 prepared according to step I, until the pH of the mixture is 5.5. The pH is measured at 50 °C.
4. Place the mixture in an oil bath at 50 °C. Start vigorous mechanical agitation using a Heidolph RZR-1 mechanical stirrer with rounded points glass propeller at 165 rpm for 48 h.
5. After this time, transfer the mixture to Falcon tubes and centrifuge it on the Hettich Universal 32 centrifuge for 20 min at 4500 rpm. Repeat centrifugation three times with two intermediate washes with distilled water.
6. The residue accumulated at the bottom of the tube is placed in an oven at 40 ºC (Scientific Series 9000) until completely dry.

Step 3 PCC HE test

1. Place about 2 g of pre-dried industrial PCC in a 400 ml beaker. Add 50 mL of ultrapure water.
2. Place in vigorous magnetic stirring to form a homogeneous suspension, with gradual heating up to 50 ° C.

3. Add the 1 M citrate buffer solution at pH 4.5 prepared according to step I, until the pH of the mixture is 5.5. The pH is measured at 50 ° C.

4. Place the mixture in an oil bath at 50 ° C.

5. Simultaneously, heat 15 mL of ultrapure water in a separate glass to 50 ºC , and adjust pH of the mixture using 0.05 M citrate buffer and pH 4.8.

6. Add to this beaker the desired amount of enzyme complex. In this case it was 1 mL.

7. Add the water + enzyme mixture to the beaker already in the oil bath and start vigorous mechanical agitation using a Heidolph RZR-1 mechanical stirrer with rounded points glass propeller at 165 rpm for 48 h.

5. After this time, transfer the mixture to Falcon tubes and centrifuge it on the Hettich Universal 32 centrifuge for 20 min at 4500 rpm. Repeat centrifugation three times with two intermediate washes with distilled water.

6. The residue accumulated at the bottom of the tube is placed in an oven at 40 ºC (Scientific Series 9000) until completely dry.

4. Methods

A variety of methods have been applied during this study in order to determine thermal behavior, chemical and physical characteristics and structure of lamellar PCC.

Following methods have been used:

- Powder X-ray diffraction analysis
- Thermogravimetry
- Evolved gas mass spectroscopy
- Solubility in water determination
- Raman spectroscopy
- Fourier transformed infrared spectroscopy
- Scanning electron microscopy
- Energy dispersive X-ray analysis

4.1. Powder X-ray diffraction analysis (PXRD)

For PXRD measurements a Bruker D-8-Advance θ-θ type with scintillation counter, energy dispersive Sol-X or position sensitive LynxEye detector and 105 position sample changer has been used. Measured range was 5° to 85.013° 2θ with a step width of 0.01°under ambient conditions. For peak identification of mineral phases, the program DiffracPlusEVA and the ICDD mineral database has been used.

4.2. Thermal analysis

4.2.1. Thermogravimetry (TGA)

For thermogravimetric measurements a unit type Mettler Toledo AG – TGA/SDTA851e was used. Around 25 mg of sample material was placed in a corundum crucible and then placed into the automated sample changer. A heating rate of 5°C per minute and an end temperature of 1100°C was set. As inert gas helium 4.0 was used to flood the heating chamber.

4.2.1. Evolved gas analysis with mass spectrometry (MS-EGA)

A unit type ThermoStar Gas Analysis System by Pfeiffer Vacuum was used to analyze the evolved gas during the TGA. A measurement with masses up to 100 amu was used to determine the main masses. The unit was then set to measure the masses of 44, 28 and 18 amu, which correspond to the masses of CO_2, CO and H_2O.

4.3. Solubility in water determination

100 mg of sample material were placed into 100 ml of distilled water to dissolve. For one batch the sample was just place into the water and for the second a magnetic stirrer with around 50 rpm was added. Four different timescales of 30 min, 2.5 h, 5 h, 24h were used to observe the dissolution process. The experiment took place under ambient conditions.

4.4. Spectroscopy

4.4.1. Raman spectroscopy

For the measurements a Horiba Jobin Yvon LabRAM-HR 800 spectrometer was used. The unit is equipped with three different lasers, a green 532 nm, a red 633nm and a blue 785 nm beam. Best results without any luminescence have been achieved with the green 532 nm laser, which showed the highest intensities for the bands.

4.4.2. Fourier transformed infrared spectroscopy (FTIR)

For FTIR measurements a Bruker Tensor 27 IR Spectrometer with Hyperion microscope was used. The unit is equipped with an ATR (attenuated total reflectance) objective which was used during the analysis. The fine sample powder was pressed down on the ATR objective to be measured. Spectrum of the measurement ranged from 400 to 8000 cm^{-1}.

4.5. Scanning electron microscopy

For scanning electron microscopy, a FEI Inspect S-50 with an ET detector (10 kV) was used.

4.6. Energy dispersive X-ray analysis (EDX)

The SEM is equipped with an energy dispersive X-ray detector type EDAX Apollo XV for quantitative analysis.

5. Results

5.1. Powder X-ray diffraction analysis (PXRD)

Preliminary of the original sample and a sample, which had been tempered at 175°C for three months, are shown in Figure 1. Comparing the PXRD data with databases and different citrates (Table 1) but no corresponding data could be found. Different citrates show some similarities, but no PXRD spectrum matches the sample’s spectrum. The sample, however, includes small amounts of calcite, which could be measured and indicated by a two-theta value of 29° 2θ. This may some residue of the manufacturing process, which included calcite.

Results also concluded, the sample only consists of a single phase, which however is not known int any database. As seen in Figure 1 tempering the sample increases its crystallinity and dis-integrates impurities from the powder.

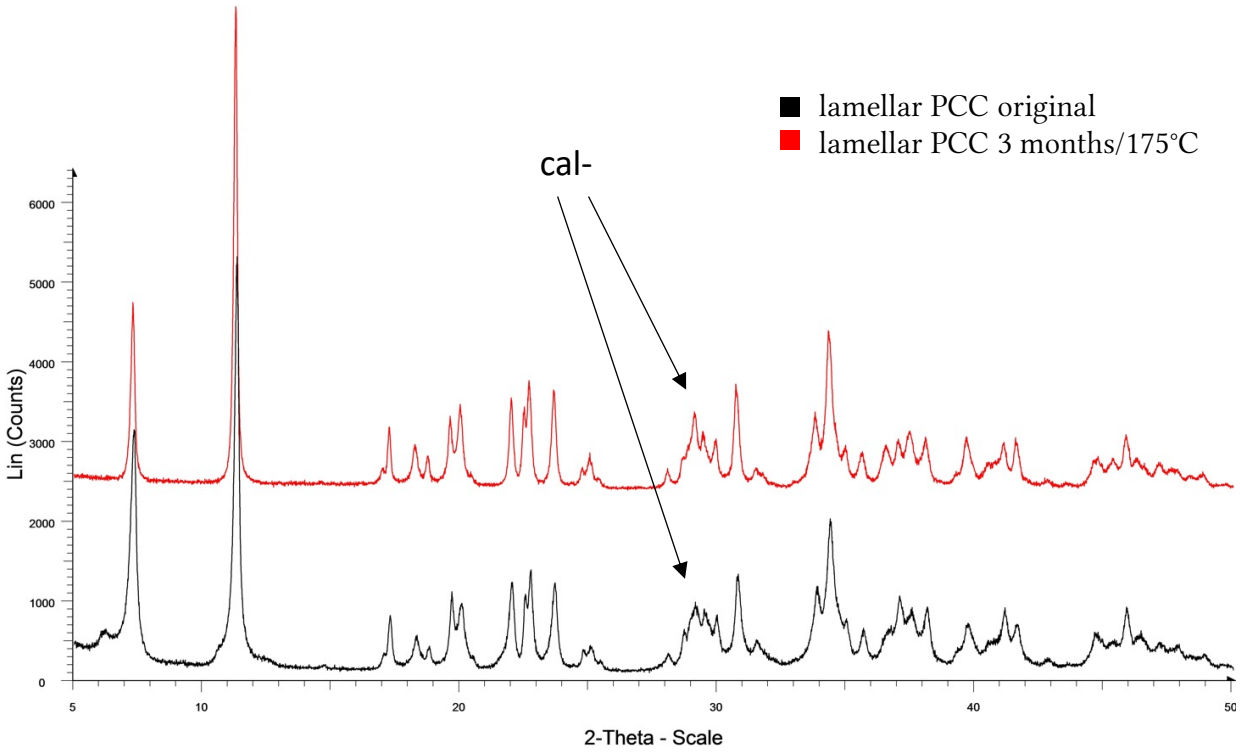

Fig. 14) PXRD pattern of lamellar PCC: upper curve (black) original sample, lower curve (red)

Table 4 list of different citrates, available for comparison to lamellar PCC

Citrat	**Formel**
Tricalcium Dicitrate Anhydrate	$(C_6H_5O_7)_2Ca_3$
Tricalcium Dicitrate Tetrahydrate	$(C_6H_5O_7)_2Ca_3$ *$4H_2O$
Tricalcium Dicitrate Hexahydrate	$(C_6H_5O_7)_2Ca_3$ *$6H_2O$
Tripotassium Citrate Monohydrate	$C_6H_5K_3O_7$ *H_2O
Trisodium Citrate Dihydrate	$C_6H_5Na_3O_7$*$2H_2O$
Trisodium Citrate Tetrahydrate	$C_6H_5Na_3O_7$*$4H_2O$
Trisodium Citrate Pentahydrate	$C_6H_5Na_3O_7$*$5H_2O$
Trirubidium Citrate Anhydrate	$C_6H_5Rb_3O_7$
Tristrontium Dicitrate Pentahydrate	$(C_6H_5O_7)_2Sr_3$ *$5H_2O$

4.7. Thermogravimetric analysis (TGA)and evolved gas analysis with mass spectrometry (MS-EGA)

In the measuring graph (Fig. 2) it can be seen that the sample degrades in multiple steps in which it emits CO2 and H2O (Fig. 3) in various amounts. A total calculated mass loss is set around 86% of its original mass. Table 2 shows consistent results of multiple TGA measurements of lamellar PCC.

The products at 475°C 24h isotherm, 500°C, 900°C, 1100°C (Fig. 4,5, 6) also have been analyzed with PXRD. At 475°C/500°C calcite and nyerereite ($NaCa(CO_3)_2$) could be detected. At 900°C it changes to around 30% portlandite ($Ca(OH)_2$), 30% disodium carbonate (Na_2CO_3) and 40% calcium oxide (CaO). At 1100°C the sample consists almost of calcium oxide however a small amount of portlandite still can be detected.

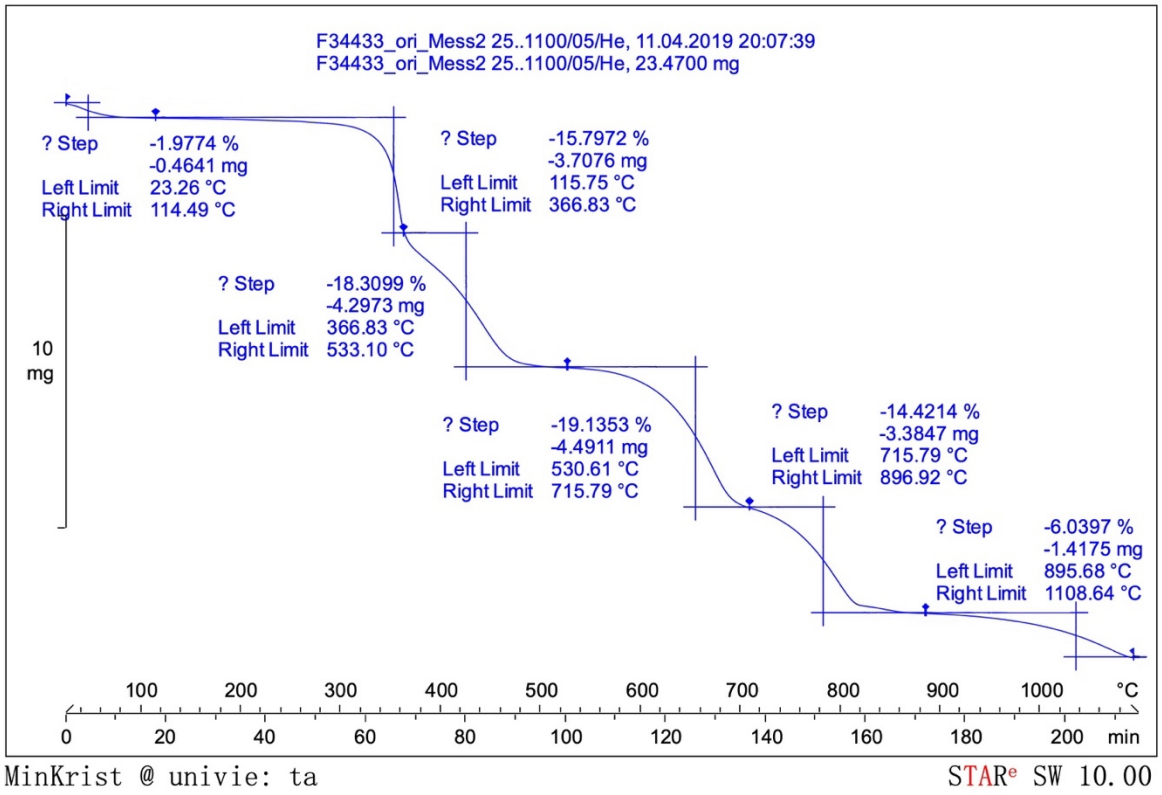

Fig. 15) TGA of lamellar PCC

Table 5 TGA measurements of lamellar PCC

TGA lamellar PCC			
sample mass: 23.4700 mg		heating rate: 5°C/min from 25° C to 1100°C	atmosphere: helium 4
step	mass loss (%)	left temperature limit	right temperature limit
1)	1.9774	23.26 °C	114.49°C
2)	15.7972	115.75°C	366.83°C
3)	18.3099	36.83°C	533.10°C
4)	19.1353	530.61°C	715.79°C
5)	14.4214	715.79°C	896.92°C
6)			
sample mass: 24.0400 mg		heating rate: 5°C/min from 25° C to 1100°C	atmosphere: helium 4
step	mass loss (%)	left temperature limit	right temperature limit
1)	1.9178	23.28°C	105.52°C
2)	15.5475	103.03°C	365.67°C
3)	18.5415	365.67°C	531.09°C
4)	19.1790	529.85°C	716.71°C
5)	14.6009	716.71°C	896.13°C
6)	6.2972	896.13°C	1108.88°C
sample mass: 24.4400 mg		heating rate: 5°C/min from 25° C to 1100°C	atmosphere: helium 4
step	mass loss (%)	left temperature limit	right temperature limit
1)	1.8736	23.37°C	105.61°C
2)	15.4556	105.61°C	366.08°C
3)	18.4487	366.08°C	530.71°C
4)	19.2345	530.71°C	716.86°C
5)	16.6738	715.57	894.51°C
6)	4.1296	896.99	1111.73°C

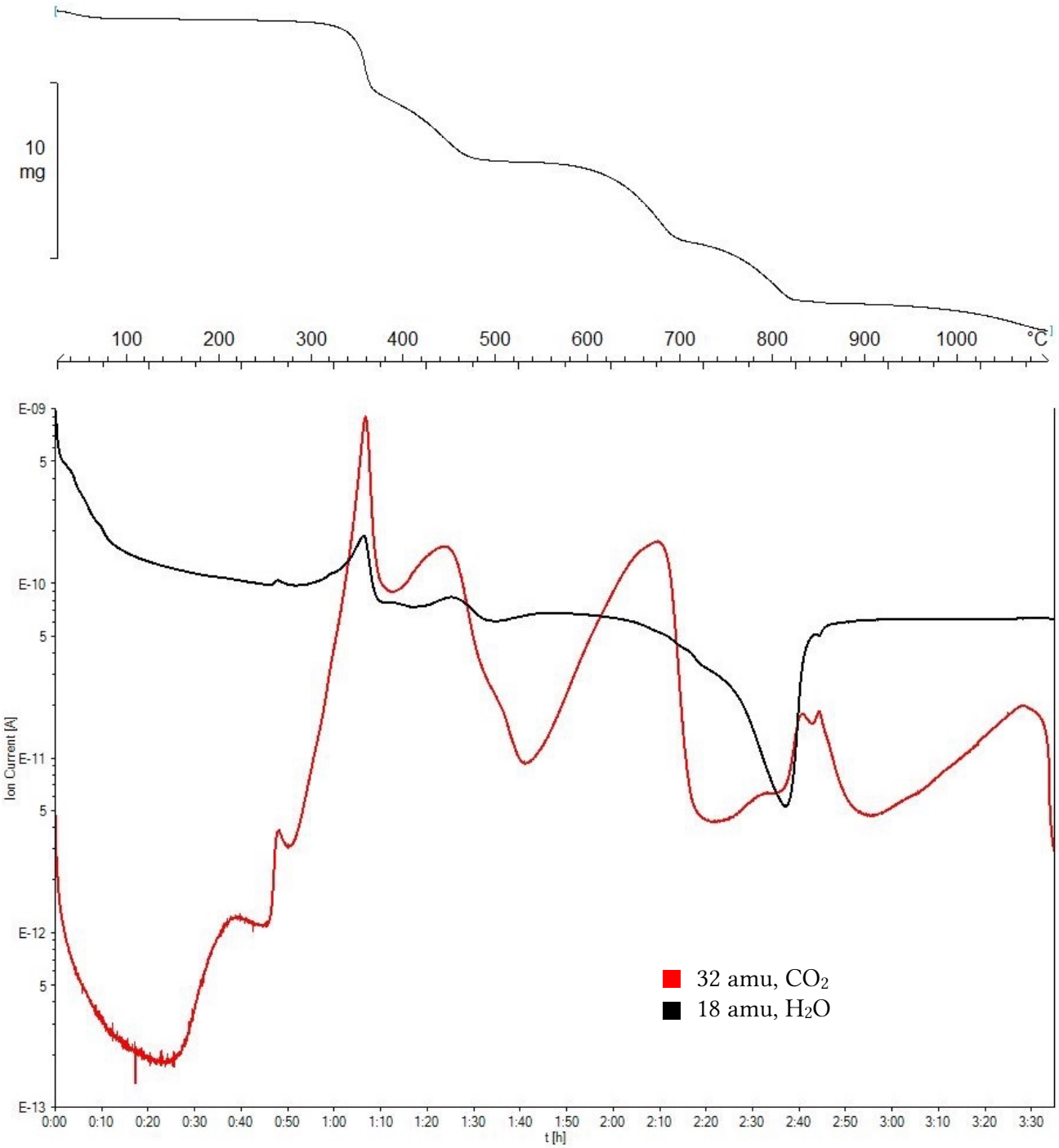

Fig. 16) TGA (upper graph) with MS-EGA of lamellar PCC: lower graph show masses of CO_2 (lower curve/ red) and H_2O (upper curve/black)

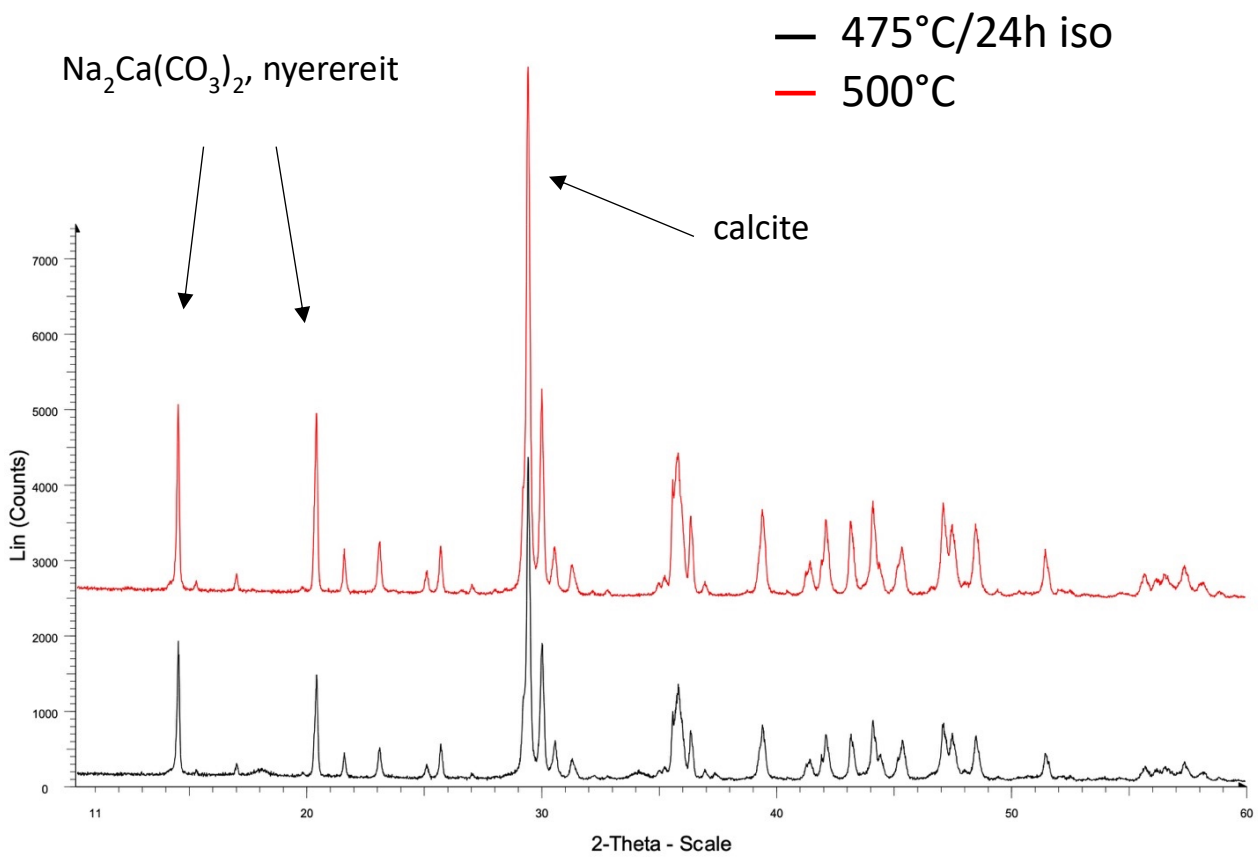

Fig. 17) PXRD pattern of lamellar PCC after TGA at 475°C and 500°C

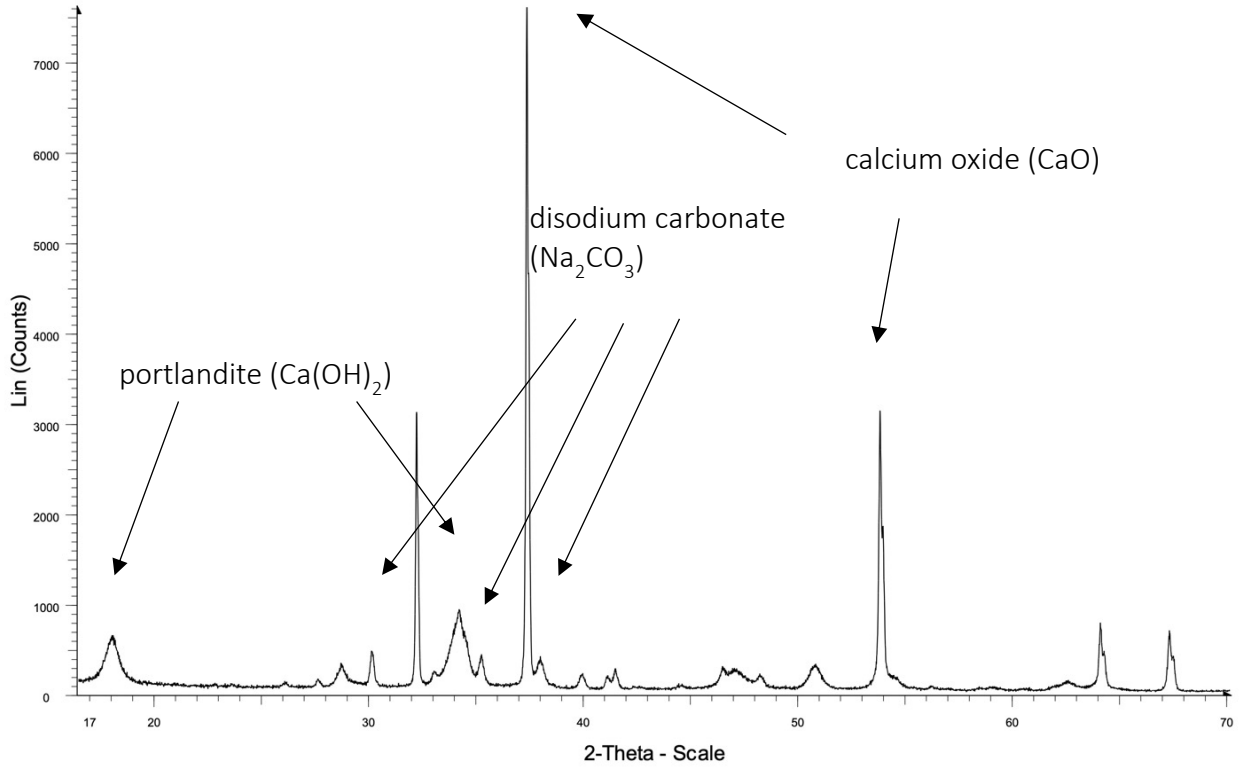

Fig. 18) PXRD pattern of lamellar PCC after TGA at 900°C

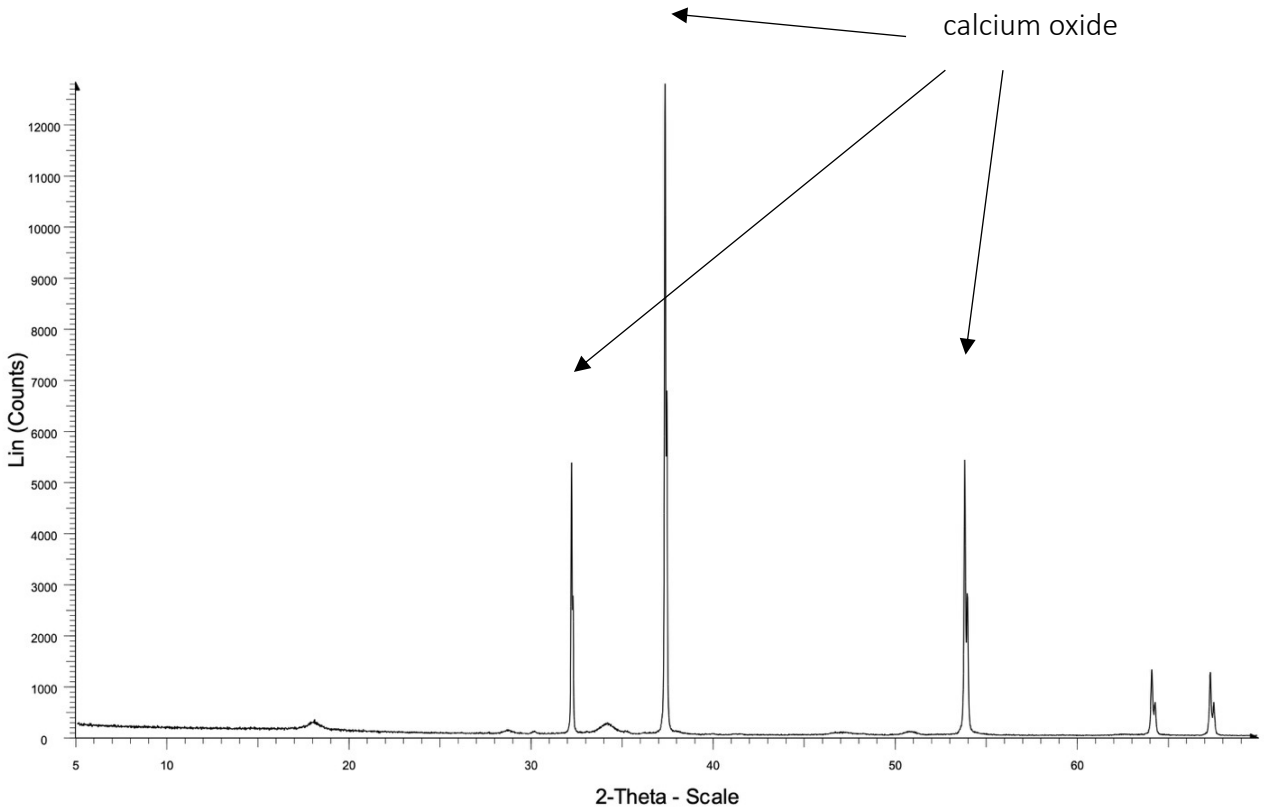

Fig. 19) lamellar PCC pattern after TGA at 1100°C

5.3. Solubility in water

The behavior of the sample with water showed, when added to water without stirring around half of it dissolves immediately, as for the residue, which settles on the bottom, it takes around 24h to fully dissolve into water. With the magnetic stirrer setup, the time it takes to fully dissolve the sample can be reduced down to three hours. In both cases the final solution can be described as slightly cloudy. When the sample have been put into the container with water a pH value of 5.5 could be measured and stays the same during the whole dissolution process. This whole process has been redone for recreation purposes.

In further investigations beakers, which include the sample which has been in the water for three and five hours without stirring, have been filtrated. Then the bottom sediment has been dried and afterwards analyzed with PXRD. The remaining solution after the filtration process has been evaporated under a laboratory vent at room temperatures, which left some crystalline substance on the ground of the glass beaker. This process took around a week until there was no water left. The crystalline substance has been then analyzed as well with PXRD. For the solution, in which the sample had been dissolved using a magnetic stirrer, this process has been also applied.

PXRD results (Fig. 7) show that the filtrate after five hours without stirring consists of the original sample and filtrated solution, which had been evaporated and crystalized, consists of citrates. The recrystallized solution of the fully dissolute sample is also made out of citrates, which shows the sample dos not recrystallize into its original composition once diluted in water.

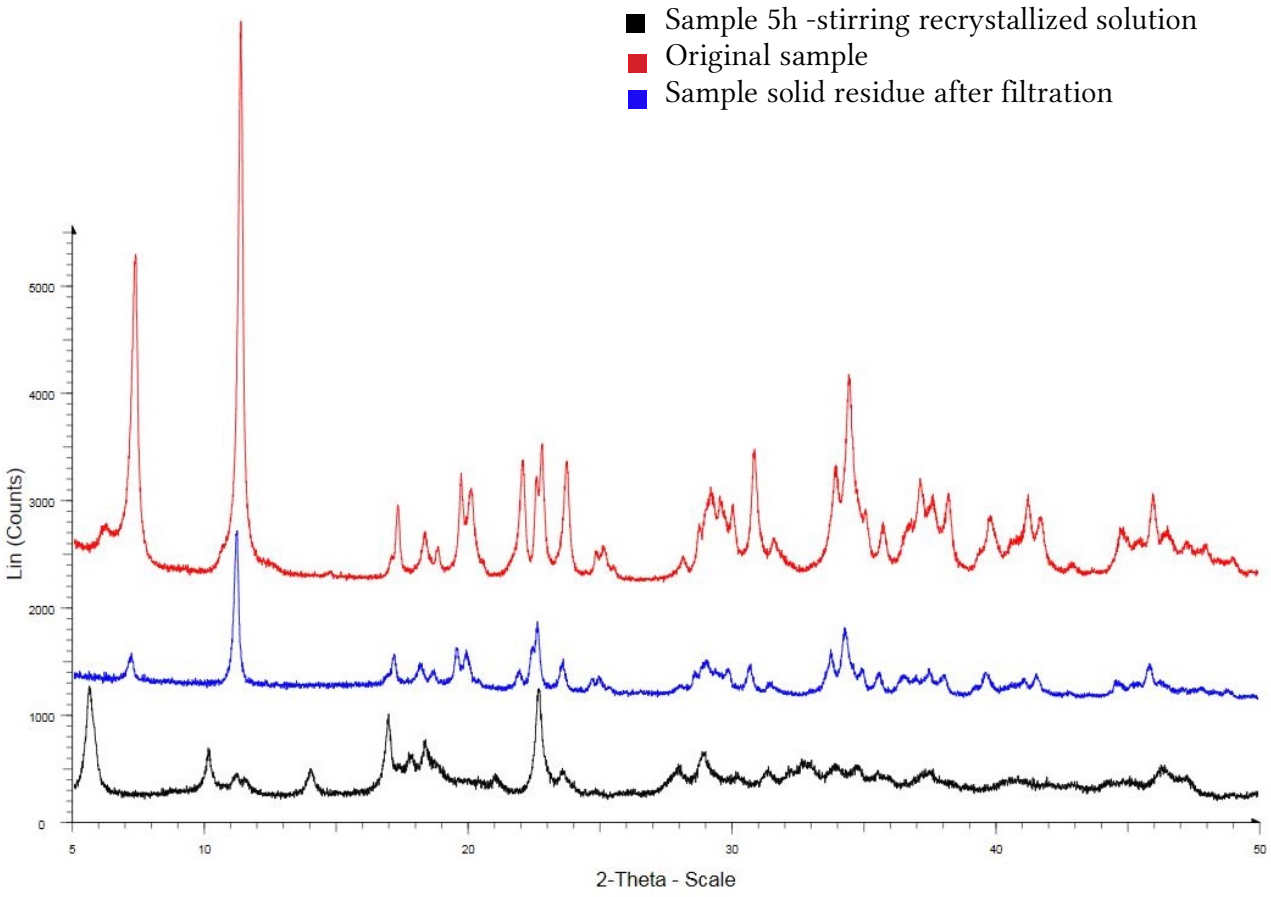

Fig. 20) PXRD pattern of the recrystallized filtrated dissolution of lamellar PCC in water for five hours without stirring and solid residue after filtration process, upper curve/red original sample, middle curve/blue sample solid residue after filtration, lower curve/black sample after 5h of stirring and recrystallized solution

5.4. Raman spectroscopy

The analysis with the Raman spectrometer, using the green 532 nm laser, shows no luminescence of the sample. Similarities to citrates can be observed comparing with databases. However, no specific substance could be determined. The sample shows also a good crystallinity.

Figure 8 shows a Raman spectrum of citric acid with the highest intensity bands at around 800 and 900 cm-1 Raman shifts. This bands can also be found on the Raman spectrum of lamellar PCC (Fig. 9) and indicate a similar composition.

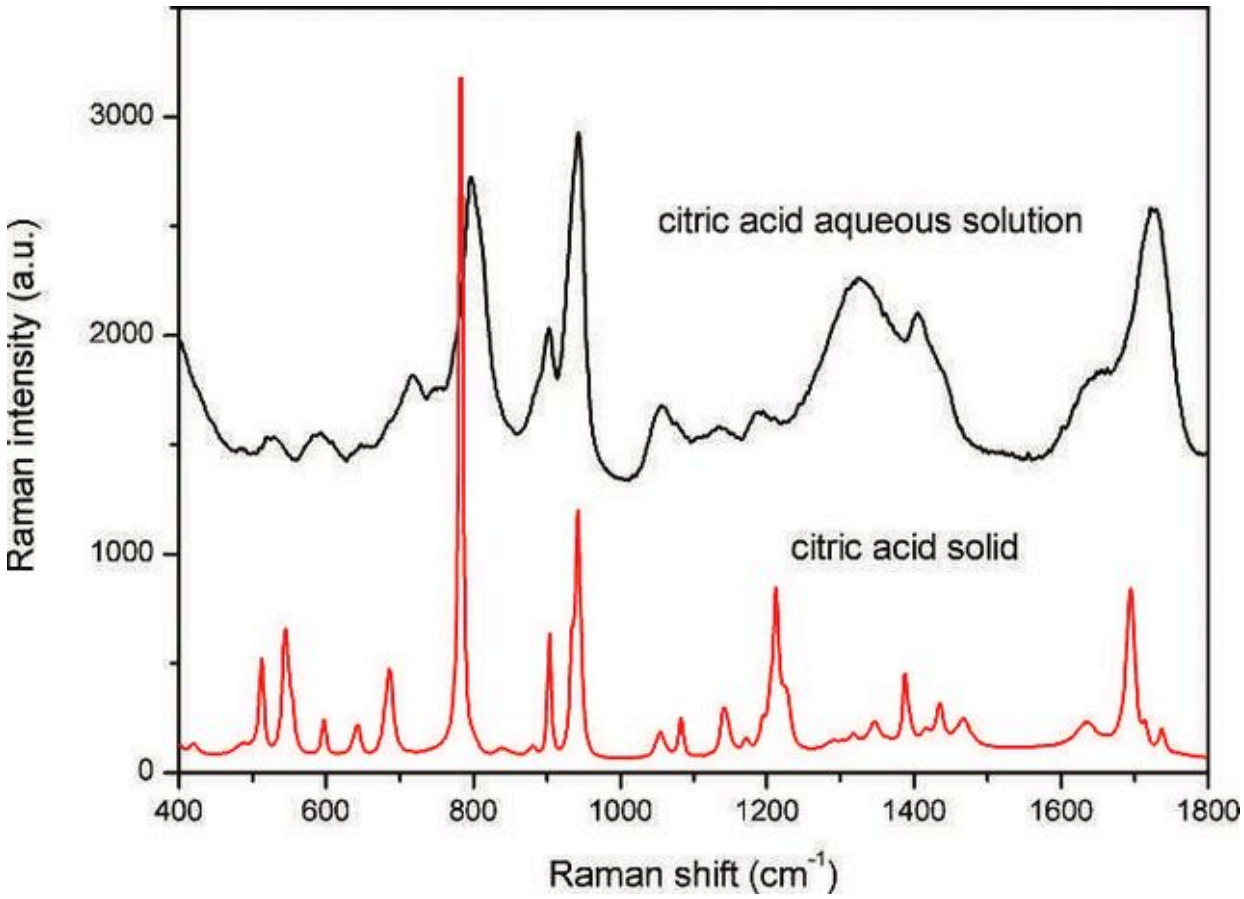

Fig. 21) Raman spectrum of citric acid in solid and aqueous form (Huang et al., 2013)

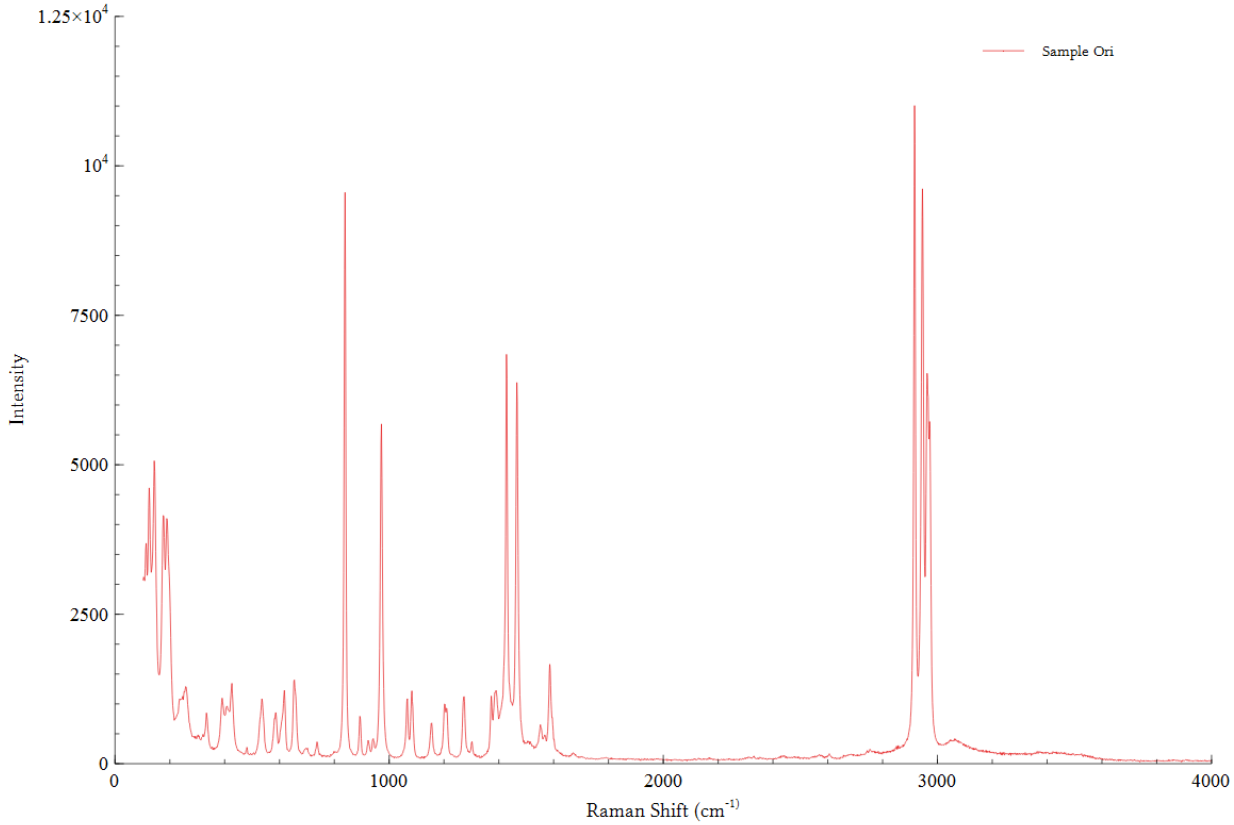

Fig. 22) Raman spectrum of lamellar PCC

5.5. Fourier transformed infrared spectroscopy (FTIR)

Results for FTIR show a spectrum in the range of 400 to 4000 cm^{-1}. . Above 4000 cm^{-1} no overtone bands of OH bonds stretching could be found, which indicates the absence of water (Fig. 10). The spectrum has been compared with databases and only one spectrum matched the sample. It is a spectrum of calcium sodium citrate ($C_6H_5CaNaO_7$) from the NIST-database (National Institute of Standards and Technology), which has been made in 1963 (Coblentz NO. 06721, 1963) (Fig. 11). As the both spectra match the main bands, which is a strong evidence the analyzed material consists of anhydrous calcium sodium citrate.

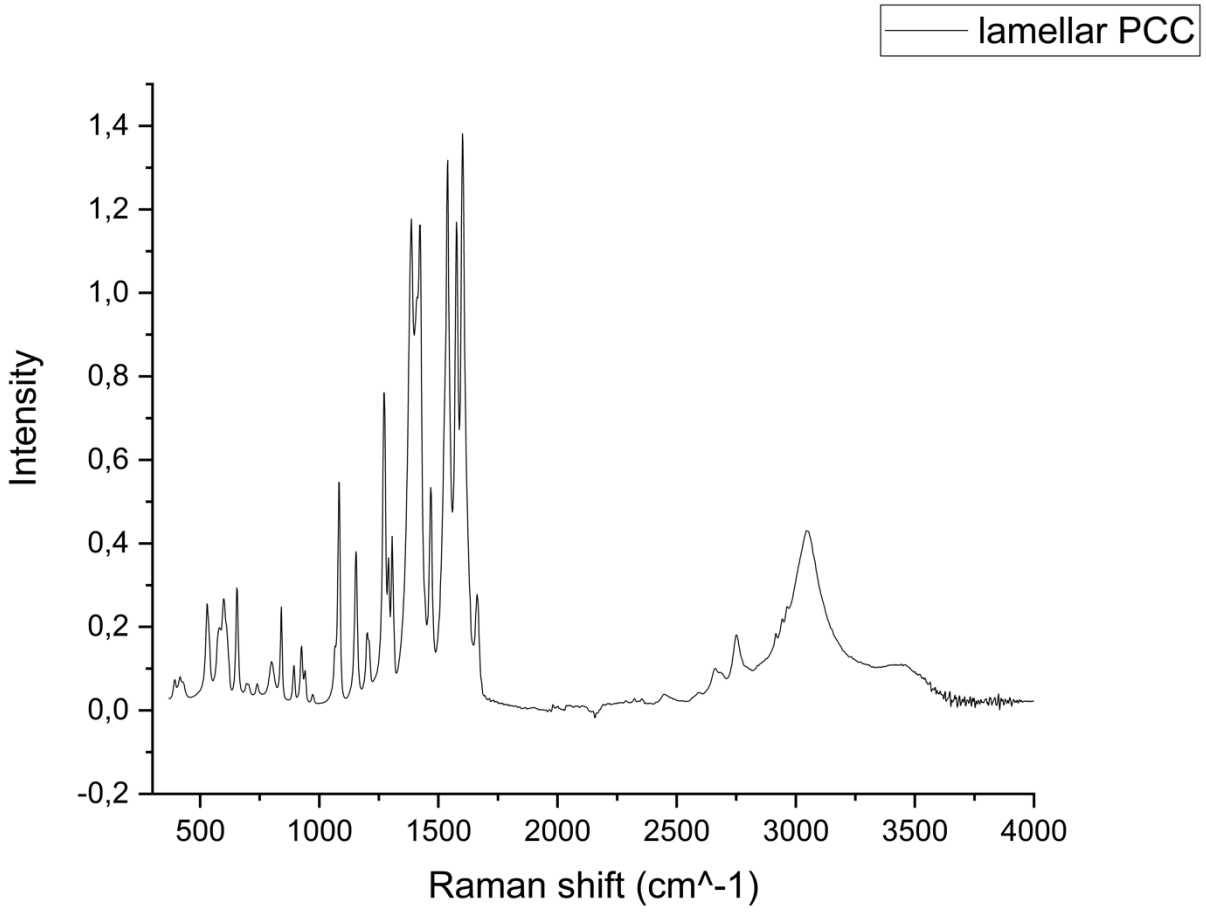

Fig. 23) FTIR-ATR spectrum of lamellar PCC

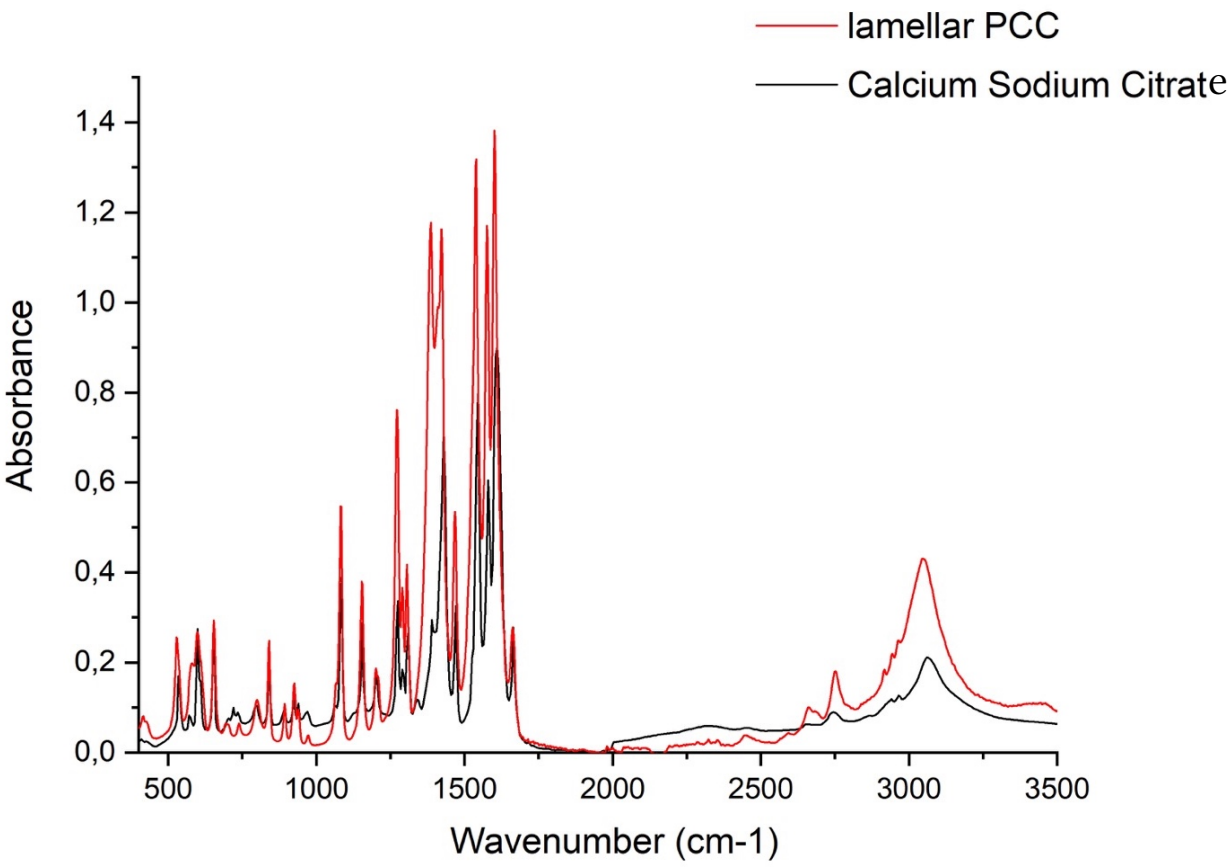

Fig. 24) lamellar PCC Spectrum (upper curve/red) compared with calcium-sodium citrate (lower curve/black) (NIST database)

5.6. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX)

In a SEM image of the sample, which had been provided prior study by Omya International AG., it could be seen, the lamellar PCC forms planar and acicular crystals (Fig.12, 13). Same results could be derived from the SEM analysis of this study and no alliteration of the powder could be observed during the time. The same planar and acicular crystals can be seen (Fig. 14, 15). Their size ranges from 2 to 10 µm in diameter.

Multiple measurements across different locations on the sample have been made, which show the main composition consists of calcium, sodium, oxygen and carbon (Fig. 16). Carbon can be neglected, as the sample had been coated with a thin layer of carbon to ensure conductivity. The results (Table 1) show a mean atom percentage of around 8.71 for Calcium and 7.20 for sodium, which represents a ratio of calcium to sodium at around 1:1. This reflects the FTIR analysis, with which calcium sodium citrate has been identified as a potential candidate for lamellar PCC with a calculated ratio of 1:1 for calcium and sodium.

Table 6 Mean values weight (wt%) and atom percentage (at%) of sodium and calcium for lamellar PCC

Na wt%	Na at%	Ca wt%	Ca at%
11.44	8.17	16.37	6.7
10.14	7.78	26.64	11.73
9.82	6.74	13.23	5.21
10.94	8.28	25.51	11.07
9.28	6.23	11.8	4.55
8.82	7.19	35.13	16.43
8.93	6.04	12.28	4.76
9.98	9.03	44.84	23.27
8.64	5.97	15.1	5.98
9.4	6.37	11.93	4.63
8.89	6.29	17.45	7.08
9.29	6.6	16.79	6.85
10.71	7.54	15.66	6.33
10.45	7.49	17.66	7.27
8.97	6.33	16.52	6.69
11.58	8.52	20.58	8.68
10.28	7.77	24.88	10.78
Mean value **9.86**	**7.20**	**20.14**	**8.71**

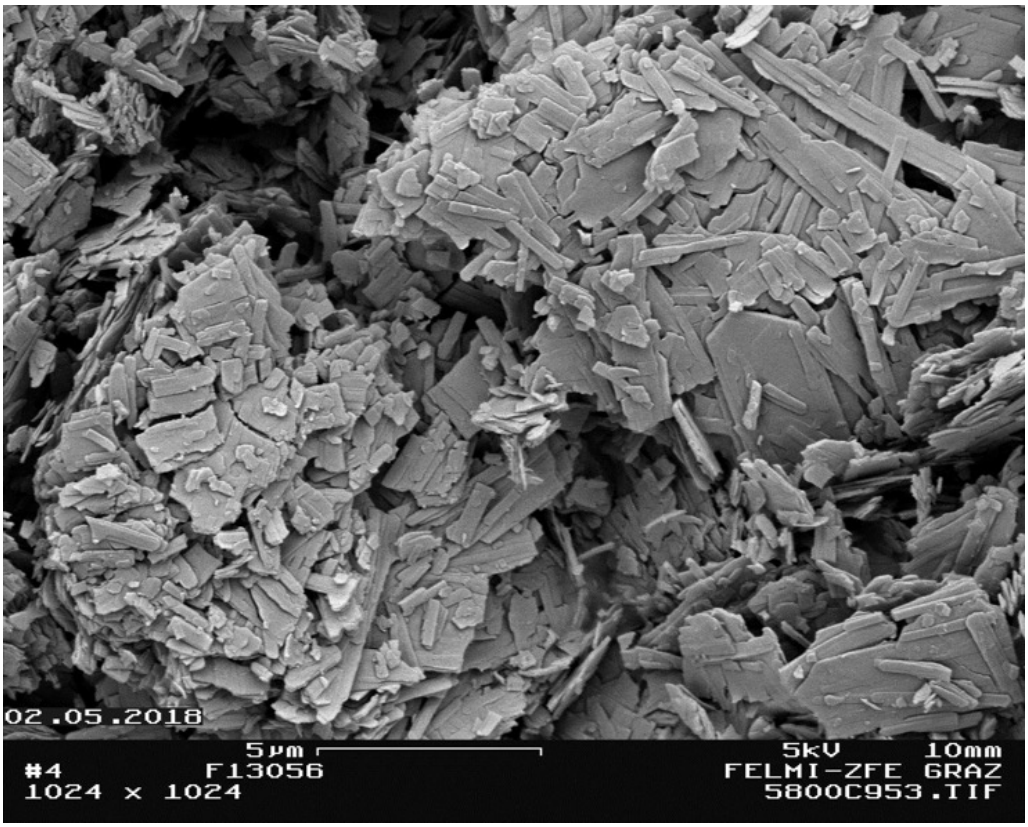

Fig. 25) SEM image of lamellar PCC provided by Omya

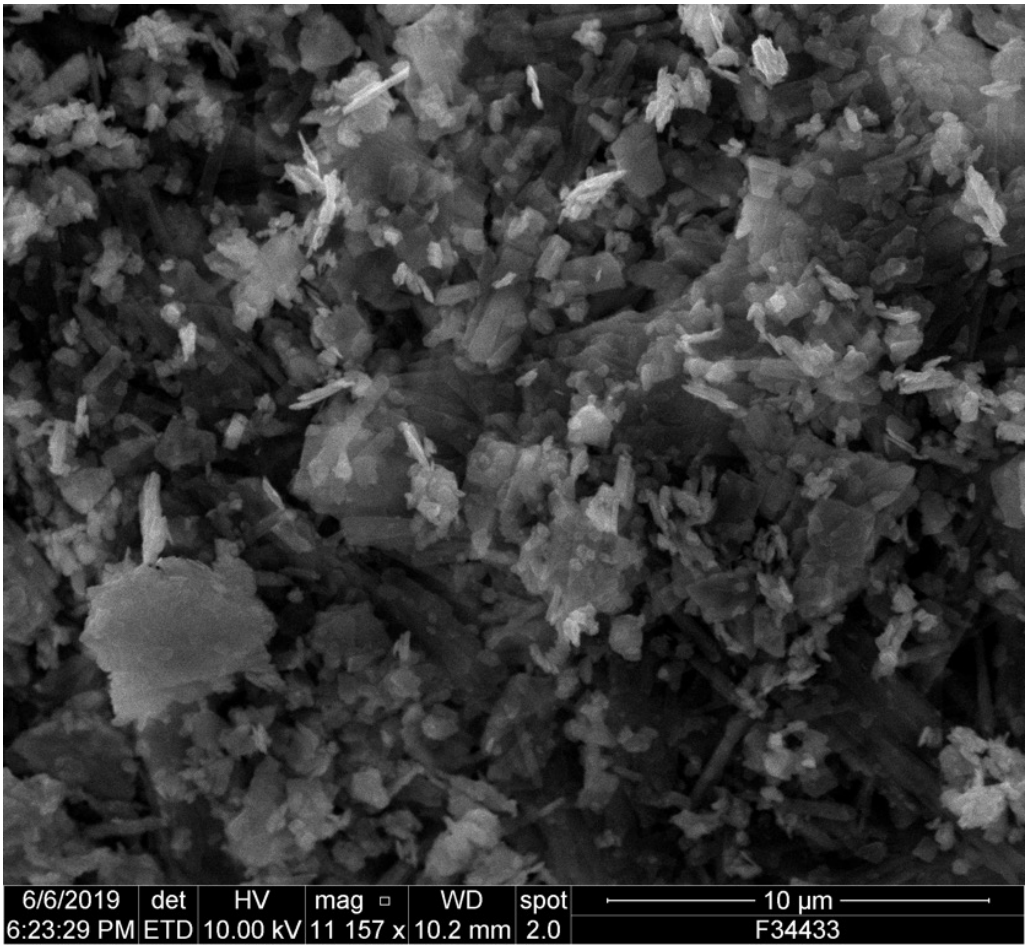

Fig. 26) SEM image of lamellar PCC

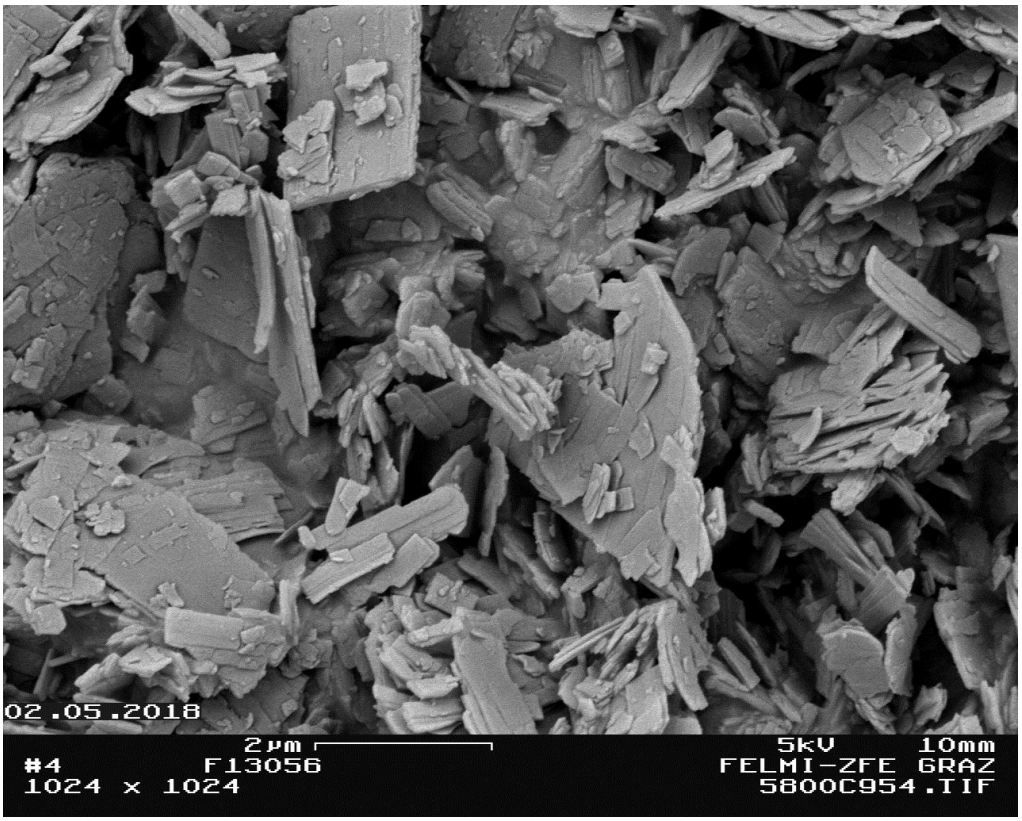

Fig. 27) SEM image of lamellar PCC provided by Omya

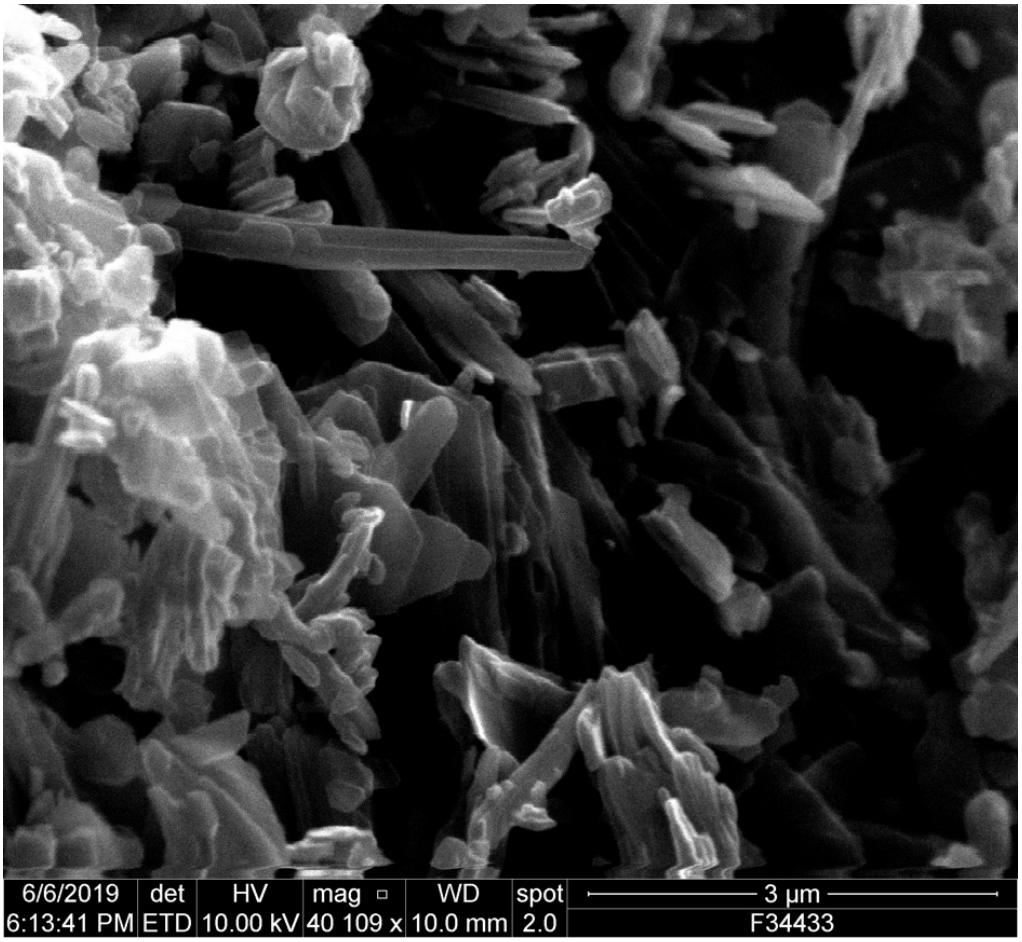

Fig. 28) SEM image of lamellar PCC

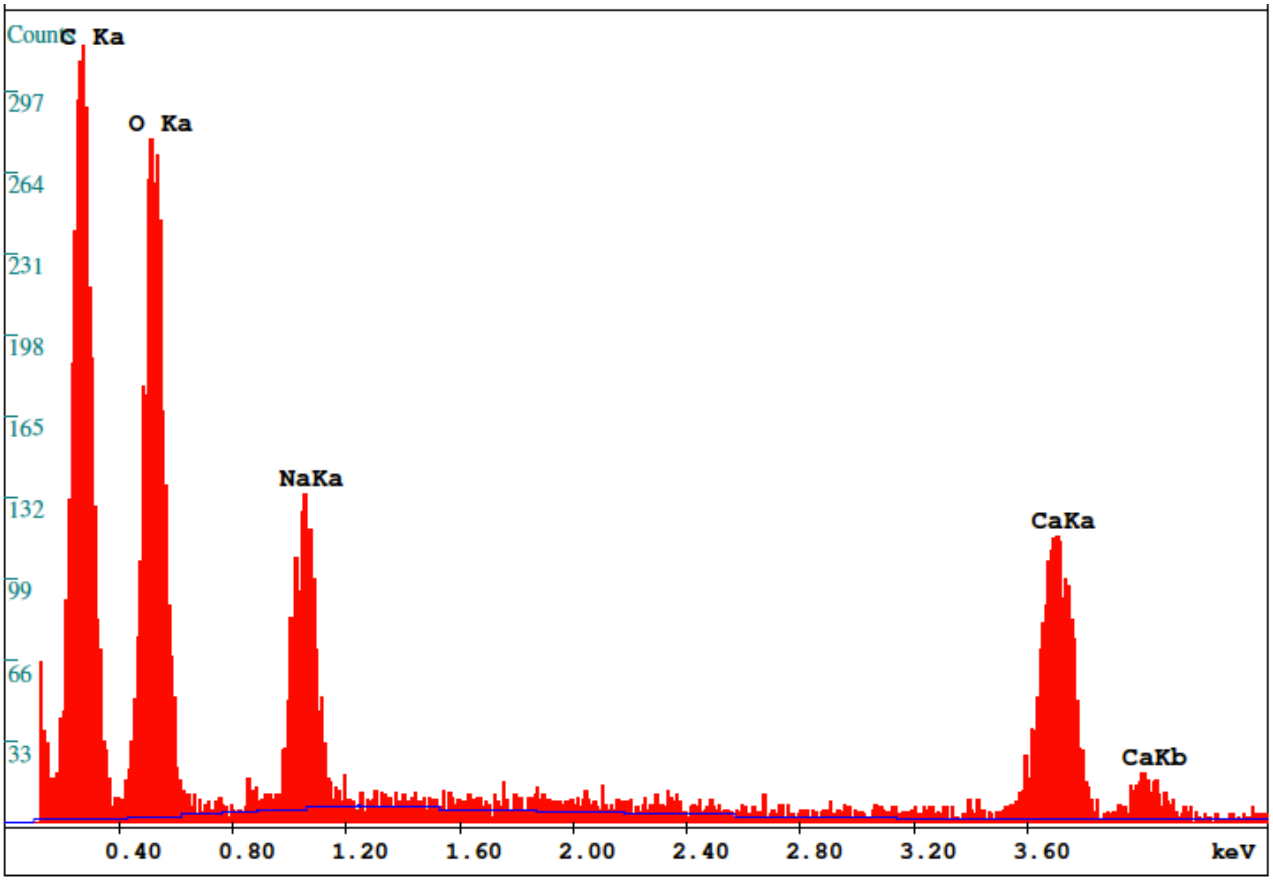

Fig. 29) EDX spectrum of lamellar PCC with main peaks of calcium and sodium

6. Discussion

Combining all the results of the measurements, a clear assumption can be made for lamellar PCC, which consists of calcium sodium citrate. The most indicative result is given by FTIR, from which one can derive a clear correlation between lamellar PCC and calcium sodium citrate. The next indicating result comes from SEM analysis via EDX, from which sodium and calcium have been determined as main cations of the substance, as well as their atomic ratio in the crystalline structure of the sample.

Taking these results and correlate them with the TGA analysis a weight loss for lamellar PCC could be calculated. Calculating and comparing these results with the measured weight loss further similarities could be identified, as the calculated weight loss is around the same value as the measured. Additionally, characteristics of the sample could be investigated such as dissolubility in water, as well as the absence of water in the sample. As there are currently no PXRD data and Raman spectra of calcium sodium citrate available, the results of this study ate the basis for future comparisons.

The structural analysis of the sample will be continued, which involves using the Riedveld method, which will reveal the first structural data of calcium sodium citrate. The collected data contribute to databases and future studies about citrates and can also be used for industrial purposes, where always new materials are searched for. Lamellar PCC could have a potential application in paper manufacturing industry due to its planar crystals.

7. Conclusion

In summary it can be said, results show, that lamellar PCC consists of calcium sodium citrate. From which is only a FTIR image known and no additional data. Main indication of the composition of the sample include FTIR and EDX. No PXRD, Raman spectroscopy and TGA data has been published yet.

In further investigations a structural analysis will be performed. All data could contribute future investigations and the characteristics of lamellar PCC demonstrates it be a potential applicant for industry purposes.

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9. List of Figures

10. List of Tables

11. List of Abbreviation