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Mechanochemical Synthesis and Characterization of Alkaline Earth Metal Terephthalates: $M(C_8H_4O_4)\cdot nH_2O$ (M = Ca, Sr, Ba)

Gudrun Scholz,*[a] Abdullah Abdulkader,[a] and Erhard Kemnitz*[a]

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Abstract. The mechanochemical synthesis offers an easy access to obtain alkaline earth metal terephthalates $M(C_8H_4O_4)\cdot nH_2O$ (M = Ca, Sr, Ba). In the presented study we describe for the first time the mechanochemical synthesis of powders of $Ca(C_8H_4O_4)\cdot 3H_2O$, $Ca(C_8H_4O_4)$, $Sr(C_8H_4O_4)\cdot H_2O$, and $Ba(C_8H_4O_4)$, which so far were only synthesized as single crystals from aqueous solutions or by reactions in an autoclave. Furthermore, a new hydrate $Ba(C_8H_4O_4)\cdot 2(1.5)H_2O$, not described so far in the literature, was prepared. All compounds were characterized by X-ray powder diffraction, thermal analysis, elemental analysis, FT-IR, and MAS NMR spectroscopic measurements.

Introduction

Seven terephthalate hydrates or terephthalates of alkaline earth metals without further chemical components or substitutions were described in the literature so far. Five of them, namely $Ca(C_8H_4O_4)\cdot 3H_2O$,[1,2] $Sr(C_8H_4O_4)\cdot 4H_2O$,[2] and $Sr(C_8H_4O_4)\cdot H_2O$,[3] as well as $Ba(C_8H_4O_4)\cdot 4H_2O$[2] and $Ba(C_8H_4O_4)$[4] were synthesized from aqueous solutions or by reactions in an autoclave for several days. As for Ca-coordination polymers introduced below, the traditional synthesis strategies for alkaline earth metal coordination polymers are either precipitations or solvothermal methods.

For $Sr(C_8H_4O_4)\cdot 3H_2O$ we reported for the first time a successful mechanochemical synthesis, and water-free $Sr(C_8H_4O_4)$ was synthesized after thermal post-treatment of the trihydrate obtained by milling.[5]

In addition, six new calcium metal-organic frameworks were described by *Lin* et al.[6] all of them have 3D structures built of polycarboxylate ligands and Ca^{2+} ions. These carboxylate ligands are BDC [1,4-benzenedicarboxylate anion ($C_8H_4O_4$)], ABDC (2-aminobenzene-1,4-dicarboxylate anion), BTC (1,3,5-benzenetricarboxylate anion), and H_2dhtp (2,5-dihydroxyterephthalate anion). These compounds were synthesized by solvothermal and microwave assisted solvothermal reactions. *N,N*-Dimethylformamide (DMF) is a terminal ligand in all compounds except one. Whereas the paper of *Lin* et al.[6] is mainly devoted to the characterization of crystal structures, *Mazaj* et al. performed a detailed study of structural dynamics of Ca(BDC)(DMF)(H_2O) induced by heating and hydration and followed changes by different spectroscopic techniques like FT-IR, MAS NMR, EXAFS, XANES.[7] They found that a thermal treatment of Ca(BDC)(DMF)H_2O) at 400 °C results in a water-free calcium terephthalate $Ca(C_8H_4O_4)$, which is transformed to $Ca(C_8H_4O_4)\cdot 3H_2O$ after exposure to a humid environment.[7]

In general, a mechanochemical synthesis of alkaline earth coordination polymers is very rarely described in the literature. Usually the authors start from metal oxides, carbonates or acetates, and explore the possibilities of liquid assisted grinding (LAG).[8–11]

In Ref. [5] we showed that phase pure $Sr(C_8H_4O_4)\cdot 3H_2O$ can be prepared very easily by milling powders of strontium hydroxide octahydrate $Sr(OH)_2\cdot 8H_2O$ with terephthalic acid (1,4-benzenedicarboxylic acid, H_2BDC) in a planetary mill.

Based on such an easy access of strontium terephthalate trihydrate by milling[5] it is the intention of the presented study to synthesize further alkaline earth terephthalates also on this mechanochemical way. Herein, the alkaline earth hydroxides and hydroxide hydrates $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$, $Ba(OH)_2\cdot H_2O$, and $Ba(OH)_2\cdot 8H_2O$ were taken as alkaline earth metal sources. The second component used for the mechanochemical reaction is, as in case of Ref. [5], terephthalic acid $C_6H_4(COOH)_2$ (H_2BDC).

All milling products are characterized by elemental analysis, X-ray diffraction (XRD), FT IR, ^{1}H- and ^{1}H-^{13}C CP MAS NMR spectroscopy, and thermal analysis.

Results and Discussion

Calcium Terephthalates $Ca(C_8H_4O_4)\cdot nH_2O$

X-ray powder diffractograms of products obtained by milling of $Ca(OH)_2$ with terephthalic acid applying different milling impacts are shown in Figure 1a–c.

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* Dr. G. Scholz
Fax: 030-2093-7277
E-Mail: Gudrun.Scholz@rz.hu-berlin.de
* Prof. Dr. E. Kemnitz
E-Mail: Erhard.Kemnitz@chemie.hu-berlin.de
[a] Department of Chemistry
Humboldt-Universität zu Berlin
Brook-Taylor-Straße 2
12489 Berlin, Germany

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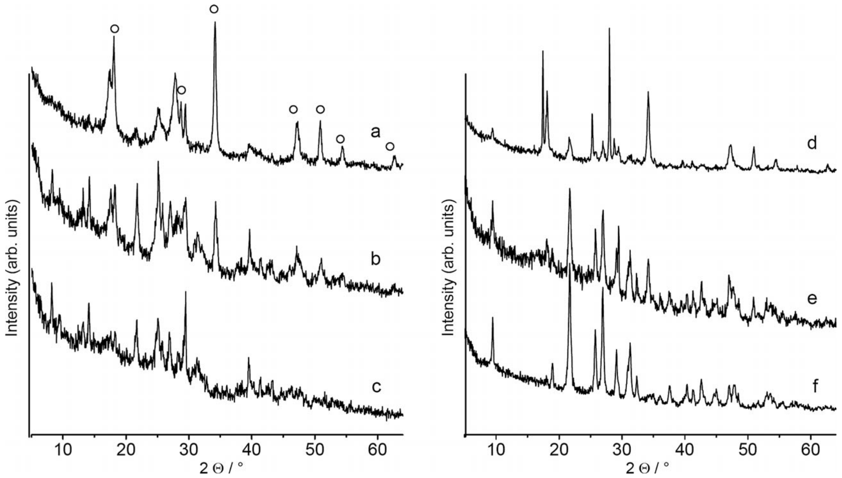


Figure 1. X-ray powder diffractograms of products obtained by milling of $Ca(OH)_2$ with terephthalic acid (H_2BDC) in a molar ratio of 1:1 applying different milling impacts: (a) 1 h milling, o: reflections of $Ca(OH)_2$, (b) 4 h milling, (c) 8 h milling; (d) 1 h milling and thermally post-treated at 300 °C, (e) 4 h milling and thermally post-treated at 300 °C, (f) 8 h milling and thermally post-treated at 300 °C.

It becomes obvious that milling time has a distinct influence on the observed reflections. After 1 h of milling the powder pattern (Figure 1a) consists only of a superposition of reflections of the precursor compounds, i.e. those of terephthalic acid (H_2BDC) and $Ca(OH)_2$ are visible (the latter are indicated). A milling time of 4 h (Figure 1b) leads to the issue of new reflections beside reflections of still visible residues of $Ca(OH)_2$ and H_2BDC. Applying the longest milling time of 8 h reflections of the precursors disappeared and only reflections of a new compound left over, however with a bad yield (poor s/n ratio, Figure 1c). Using pre-milled starting materials did not improve this situation.

A thermal post-treatment of the milled products for 2 h at 300 °C shows that the original short milling (1 h) did not induce any chemical reaction. Here, well crystalline precursor compounds can be identified (Figure 1d). This situation changes for the samples treated before with higher milling impacts. New, but for both samples identical reflections, appeared after the thermal post-treatment (Figure 1e, f). These powder diffractograms (Figure 1e, f) are completely in agreement with the powder pattern given for Ca-BDC(400) in the literature,[7] which corresponds to the water-free calcium terephthalate $Ca(C_8H_4O_4)$. It means, the thermal post-treatment of the products obtained by milling with higher impact results in the formation of the water-free calcium terephthalate $Ca(C_8H_4O_4)$.

Usually, during a thermal post-treatment up to 300 °C only a water release can be expected (for comparison see also Figure S2, Supporting Information). Following that, the powder pattern of the milling product shown in Figure 1c, i.e. the precursor before thermal annealing, should be a calcium terephthalate hydrate. However, the water content of $Ca(OH)_2$ used as starting material for milling is obviously too low to give a well crystalline product already after milling. In such a case adding small amounts of water, i.e. performing liquid assisted grinding, should result in a desired hydrate.

X-ray powder diffractograms of products obtained by milling of $Ca(OH)_2$ with H_2BDC and addition of few microliters of H_2O are depicted in Figure 2. From these powder patterns it is evident that a well crystalline product is formed and longer milling times are not necessary (see for comparison Figure 2a, b). Moreover, the obtained powder pattern is identical to the powder pattern given for $Ca(C_8H_4O_4)\cdot 3H_2O$[7] and is almost in agreement with the powder pattern recalculated from single crystal data of $Ca(C_8H_4O_4)\cdot 3H_2O$ (Figure 2d), although the relative intensities of reflections are slightly changed.

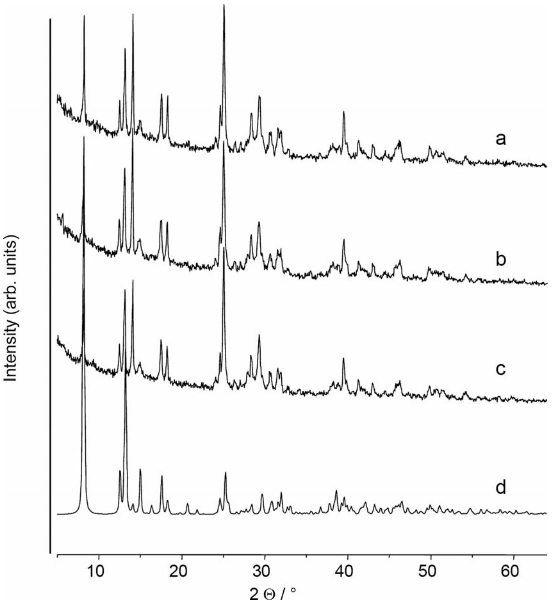


Figure 2. X-ray powder diffractograms of products obtained by milling of $Ca(OH)_2$ with H_2BDC (1:1) and addition of (a) 130 µL H_2O (1 h milling), (b) 130 µL H_2O (4 h milling), (c) 170 µL H_2O (1 h milling), (d) powder diffractogram of $Ca(C_8H_4O_4)\cdot 3H_2O$, recalculated from single crystal data.

Therefore we can conclude that milling of $Ca(OH)_2$ with H_2BDC for only 1 h under addition of small portions of water (LAG) results in the formation of $Ca(C_8H_4O_4)\cdot 3H_2O$, which transforms into $Ca(C_8H_4O_4)$ after calcinations at 300 °C (the same powder pattern as shown in Figure 1f is obtained).

Both FT-IR spectra (Figure S1, Supporting Information) as well as DTA-TG measurements (Figure S2, Supporting Information), along with elemental analysis (Table S1, Supporting Information) clearly show the formation of trihydrated and dehydrated phases of Ca-terephthalate, respectively. For all methods mentioned an almost theoretical ideal behavior is observed. For instance, the TG curve of $Ca(C_8H_4O_4)\cdot 3H_2O$ (Figure S2) shows – due to the liberation of water (m18) – a mass loss of 19.8 % in the first step up to 200 °C, which is quite close to the theoretically expected loss of 20.9 %. As expected, the water-free compound shows nearly no mass loss in that temperature region. The decomposition of the compounds starts above 400 °C evidenced by the release of CO_2 in a two-step process (m44, Figure S2).

^1H-^{13}C CP MAS NMR spectra of $Ca(C_8H_4O_4)\cdot 3H_2O$ and $Ca(C_8H_4O_4)$ prepared by milling (LAG) and consecutive thermal treatment are shown in Figure 3. In both cases, the MAS NMR spectra are in agreement with those from the literature.[7] The spectrum shown in Figure 3b for $Ca(C_8H_4O_4)$ is identical to that of Ca-BDC(400).[7] It shows only three signals: one signal at δ = 173.6 ppm for carboxyl carbon atoms, and two signals (δ =137 ppm and 131.6 ppm) belonging to aromatic carbon atoms.

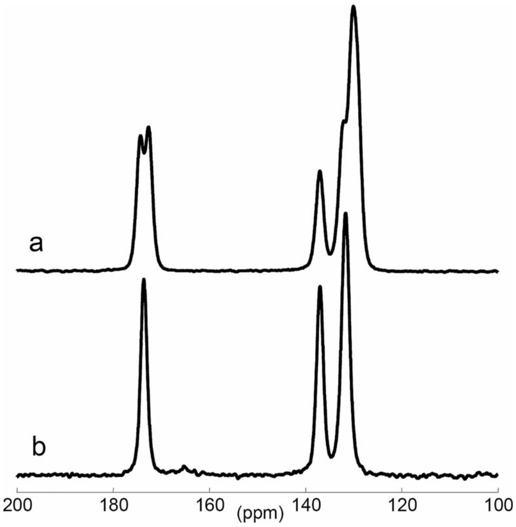


Figure 3. ^1H-^{13}C CP MAS NMR spectra of (a) $Ca(C_8H_4O_4)\cdot 3\ H_2O$, and (b) $Ca(C_8H_4O_4)$ prepared by milling $Ca(OH)_2$ with H_2BDC and 170 µL H_2O for 1 h (a) and subsequent thermal treatment at 300 °C (b).(ν_{rot} = 10 kHz, p15 = 6 ms).

For $Ca(C_8H_4O_4)\cdot 3H_2O$ signals for two different carboxylate groups appear at δ = 174.3 ppm and 172.7 ppm, accompanied by an additional signal for an aromatic carbon at δ = 130 ppm (Figure 3a). This is a consequence of the 3D structure of $Ca(C_8H_4O_4)\cdot 3H_2O$ with CaO_8 chains, which was discussed in detail in the literature.[2,7] ^1H-^{13}C CP MAS NMR spectra of both compounds show a distinct dependence of relative signal intensities on the contact time (cf. Figure S3). The magnetization transfer from ^1H to ^{13}C is generally in favor of more distant carbon atoms if larger contact times (here p15) are applied. This can be unambiguously observed comparing the relative intensity ratio of ^{13}C signals of carboxyl carbon atoms with those of aromatic carbon atoms (cf. Figure S3, Supporting Information).

Attempts to grow single crystals from powders obtained after milling [$Ca(C_8H_4O_4)\cdot 3H_2O$] and thermal post-treatment [$Ca(C_8H_4O_4)$], respectively, were so far not successful.

Strontium Terephthalates $Sr(C_8H_4O_4)\cdot nH_2O$

Four strontium terephthalates (hydrates) are described in the literature: we prepared $Sr(C_8H_4O_4)\cdot 3H_2O$ by milling of $Sr(OH)_2\cdot 8H_2O$ with terephthalic acid for only 1 h and obtained in addition $Sr(C_8H_4O_4)$ after thermal post-treatment.[5] Furthermore, the monohydrate $Sr(C_8H_4O_4)\cdot H_2O$ is known, which was prepared by solvothermal reaction for 7 d, published in 2011.[3] With $Sr(C_8H_4O_4)\cdot 4H_2O$[2] the list of strontium terephthalates is completed.

In the presented study we elaborated the conditions for the successful mechanochemical synthesis of $Sr(C_8H_4O_4)\cdot 3H_2O$ starting from $Sr(OH)_2\cdot 8H_2O$. In addition, the water free hydroxide $Sr(OH)_2$ was used as a new precursor compound.

Evaluation of Successful Conditions for Mechanochemical Synthesis of $Sr(C_8H_4O_4)\cdot 3H_2O$

Whereas in Ref. [5] the mechanochemical synthesis and structure of $Sr(C_8H_4O_4)\cdot 3H_2O$ were described, the conditions for a successful synthesis by milling in a planetary mill were studied in more detail and will be summarized very briefly. This includes the variation of molar ratios of starting substances, the variation of milling impacts down to the use of a mortar, or liquid assisted grinding experiments with CH_3OH to eliminate water.

The molar ratios used for milling $Sr(OH)_2\cdot 8H_2O$ with H_2BDC were varied from 1:0.25 up to 1:2. We found that the two precursors react stoichiometrically with each other. Reflections of $Sr(C_8H_4O_4)\cdot 3H_2O$ are even visible with the lowest supply of terephthalic acid, accompanied by still visible reflections of excess $Sr(OH)_2\cdot 8H_2O$. The powder pattern indicates phase pure $Sr(C_8H_4O_4)\cdot 3H_2O$ for the ratio 1:1, and in combination with elemental analysis an excess of H_2BDC can be proven for higher proportions in the mixture.

As shown in Ref. [5] within 1 h of milling $Sr(C_8H_4O_4)\cdot 3H_2O$ had been formed. However, further tests demonstrated that even with a milling time of only 15 min the reaction was complete. But the impact of a planetary mill (see Experimental Section) was still necessary. Attempts by simply grinding the two precursors in a mortar were not successful.

Our previous experiments clearly indicated the formation of $Sr(C_8H_4O_4)$ after thermal treatment of mechanochemically synthesized $Sr(C_8H_4O_4)\cdot 3H_2O$. Attempts to remove the water directly by milling to obtain $Sr(C_8H_4O_4)$ by adding only few droplets of methanol (LAG) failed. The presence of the solvent manifests only in a worse crystallinity of $Sr(C_8H_4O_4)\cdot 3H_2O$, i.e. $Sr(C_8H_4O_4)$ was not formed. On the other hand the mechanochemically synthesized $Sr(C_8H_4O_4)\cdot 3H_2O$ was successfully recrystallized from water and cubic colorless crystals were formed. X-ray structure analysis of these single crystals proved the formation of $Sr(C_8H_4O_4)\cdot 4H_2O$, which is obviously the most stable phase of strontium terephthalate hydrates, instead of the expected $Sr(C_8H_4O_4)\cdot 3H_2O$. All structure data are identical to previously published results for $Sr(C_8H_4O_4)\cdot 4H_2O$.[2] It means on the other hand that the mechanochemical synthesis is the only possibility to obtain $Sr(C_8H_4O_4)\cdot 3H_2O$ with locally formed (SrO_8) polyhedra. After recrystallization the local coordination changes from (SrO_8) to (SrO_{10}) (for comparison see Refs. [2,5]).

Mechanochemical Experiments with $Sr(OH)_2$

So far, all of our milling experiments were performed with $Sr(OH)_2\cdot 8H_2O$ as source for Sr^{2+} cations. $Sr(C_8H_4O_4)\cdot 3H_2O$ and $Sr(C_8H_4O_4)$ were accessible on this way, but the monohydrate, also described in Ref. [3] was never formed during a mechanochemical reaction.

Therefore, further milling experiments were performed with the commercially available water-free hydroxide $Sr(OH)_2$ and terephthalic acid (H_2BDC). With a chosen molar ratio of 1:1 [$Sr(OH)_2$:H_2BDC] and milling times of one and four hours, respectively, we instantly obtained new powder patterns. Reflections of the starting materials disappeared and the new reflections, depicted in Figure 4a, completely agree with the powder pattern of $Sr(C_8H_4O_4)\cdot H_2O$, recalculated from single crystal data given in Ref. [3] (Figure 4b). The product obtained after 1 h of milling shows a worse crystallinity and is not implemented in Figure 4. Attempts to induce a reaction manually in a mortar were not favorable. Choosing a molar ratio of 1:2 [$Sr(OH)_2$:H_2BDC] the Sr-terephthalate monohydrate is also formed, but expectedly, reflections belonging to un-consumed H_2BDC are still visible in the powder diffractogram (not shown here).

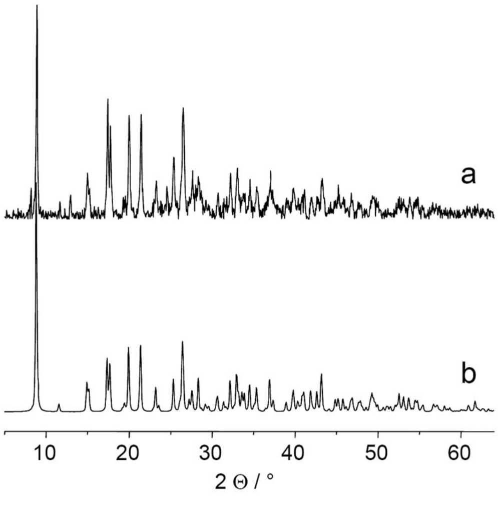


Figure 4. X-ray powder diffractograms of the product obtained by milling of $Sr(OH)_2$ with H_2BDC (molar ratio: 1:1) for 4 h (a) and of $Sr(C_8H_4O_4)\cdot H_2O$ (b), recalculated from single crystal data.

The thermoanalytical curves (cf. Figure S4, Supporting Information) demonstrate a two-step water release below 200 °C, accompanied by mass loss of 7.6 %, which is close to the expected theoretical mass loss of 6.7 % of $Sr(C_8H_4O_4)\cdot H_2O$. These findings are assisted by the carbon and hydrogen contents determined by elemental analysis (Table S1, Supporting Information). The decomposition of the monohydrate starts around 500 °C in one step (release of CO_2, m44).

The ^1H-^{13}C CP MAS NMR spectrum of $Sr(C_8H_4O_4)\cdot H_2O$ (Figure 5) is completely embedded in the spectral patterns recorded for $Sr(C_8H_4O_4)\cdot 3H_2O$ and $Sr(C_8H_4O_4)$ (Figure 5). The spectra of the latter two compounds were also shown in Ref. [5] for a different contact time.

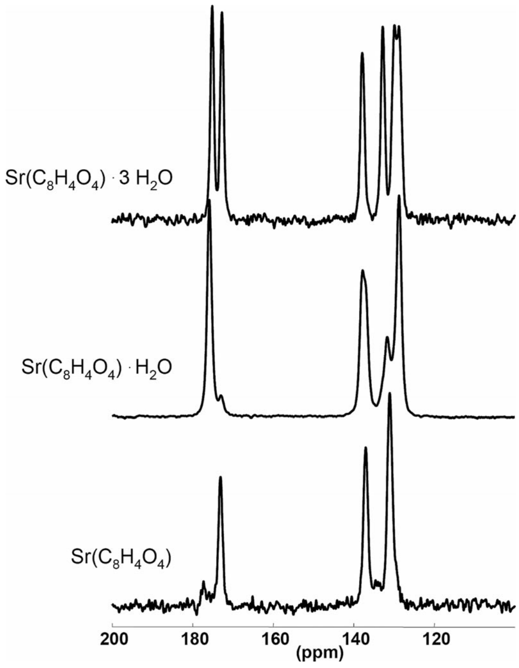


Figure 5. ^1H-^{13}C CP MAS NMR spectrum of $Sr(C_8H_4O_4)\cdot H_2O$, prepared by milling $Sr(OH)_2$ with H_2BDC (molar ratio: 1:1) for 4 h. For comparison, the spectra of $Sr(C_8H_4O_4)\cdot 3H_2O$ and $Sr(C_8H_4O_4)$, already shown in Ref. [5] for another contact time, are added. (ν_{rot} = 10 kHz, p15 = 6 ms).

Two carbon signals with quite different intensity belong to carboxyl groups (δ =175.8 ppm, 172.8 ppm), and three sites were resolved for aromatic carbon atoms (δ =137.8 ppm, 131.6 ppm, 128.7 ppm) for $Sr(C_8H_4O_4)\cdot H_2O$. Comparing ^1H-^{13}C CP MAS NMR spectra of $Sr(C_8H_4O_4)\cdot H_2O$ with those of the trihydrate and the water-free compound (Figure 5), the signals at δ = 175.8 ppm and 128.7 ppm can be assigned to more strongly hydrogen bridged carboxyl carbon and aromatic carbon atoms, respectively. ^{13}C signal intensities recorded for $Sr(C_8H_4O_4)\cdot H_2O$ show a similar dependence on contact times as shown for the calcium terephthalate compounds in Figure S3.

The FT IR spectra too are quite similar to those shown in the supporting information in Ref. [5] for $Sr(C_8H_4O_4)\cdot 3H_2O$ and $Sr(C_8H_4O_4)$. The fraction of broad vibration bands above 3000 cm^{-1} lies, as expected, for the monohydrate, between those of the trihydrate and the water-free compound. For completeness, the FT IR spectrum of $Sr(C_8H_4O_4)\cdot H_2O$ is shown in the Supporting Information (Figure S5).

Whereas the mechanochemical synthesis of $Sr(C_8H_4O_4)\cdot H_2O$ just by milling for 4 h performs well starting from $Sr(OH)_2$ and H_2BDC, the synthesis of a Ca-terephthalate was unsuccessful under the same conditions. From this, for Barium, as an even larger alkaline earth metal cation, an easy and fast access to Ba-terephthalates applying even shorter milling times should be expected.

Barium Terephthalates $Ba(C_8H_4O_4)\cdot nH_2O$

From the literature two Ba-terephthalate compounds are known. These are the water-free $Ba(C_8H_4O_4)$,[4] and $Ba(C_8H_4O_4)\cdot 4H_2O$.[2] In both cases the single crystals were grown from aqueous solution, and their mechanochemical synthesis was not described so far. Our mechanochemical experiments aimed at the formation of $Ba(C_8H_4O_4)$ or $Ba(C_8H_4O_4)\cdot nH_2O$ compounds.

We started from $Ba(OH)_2$, $Ba(OH)_2\cdot H_2O$, and $Ba(OH)_2\cdot 8H_2O$ as sources for Ba^{2+} ions, which all are commercially available, and milled them with terephthalic acid. XRD powder patterns of products obtained by milling of barium hydroxides or hydroxide hydrates with terephthalic acid are collected in Figure 6.

As deduced above, using $Ba(OH)_2$ 1 h of milling is already sufficient to obtain reflections, which are different to those of the starting materials (Figure 6a). The same set of reflections was obtained using $Ba(OH)_2\cdot H_2O$ as reactant and a milling time of 4 h (Figure 6b). The reaction with $Ba(OH)_2\cdot H_2O$ is also successful after 1 h of milling, however the longer milling time results here in a better crystallinity. A comparison of these powder patterns with the powder diffractogram of $Ba(C_8H_4O_4)$, recalculated from single crystal data from Ref. [4] (Figure 6c), gives unambiguous evidence for the formation of the water-free barium terephthalate $Ba(C_8H_4O_4)$.

These structural findings are supported by thermoanalytical measurements. DTA-TG curves of the milling products display an only marginal mass loss of about 3 % near 300 °C (Figure S6, Supporting Information) in the case of $Ba(OH)_2$ as precursor. Using $Ba(OH)_2\cdot H_2O$ as precursor, the mass loss is a bit higher (≈ 6 %) and corresponds to the loss of one water molecule assuming formally a formula of $Ba(C_8H_4O_4)\cdot H_2O$ (Figure S6b). The release of water does not occur not below 300 °C, which is high compared to Ca- and Sr-terephthalates (cf. Figure S2a, Figure S4, and Figure 2 in Ref. [5]). However, with the knowledge of the crystalline phases identified in both cases as $Ba(C_8H_4O_4)$ (Figure 6a–c) residues of water or even residues of X-ray amorphous hydroxides might be assumed to be present in the sample (Figure 6b, Figure S6b). The latter may also explain small deviations in the carbon and hydrogen contents for the mechanochemically synthesized $Ba(C_8H_4O_4)$ samples (Table S1), which were both found to be slightly too low.

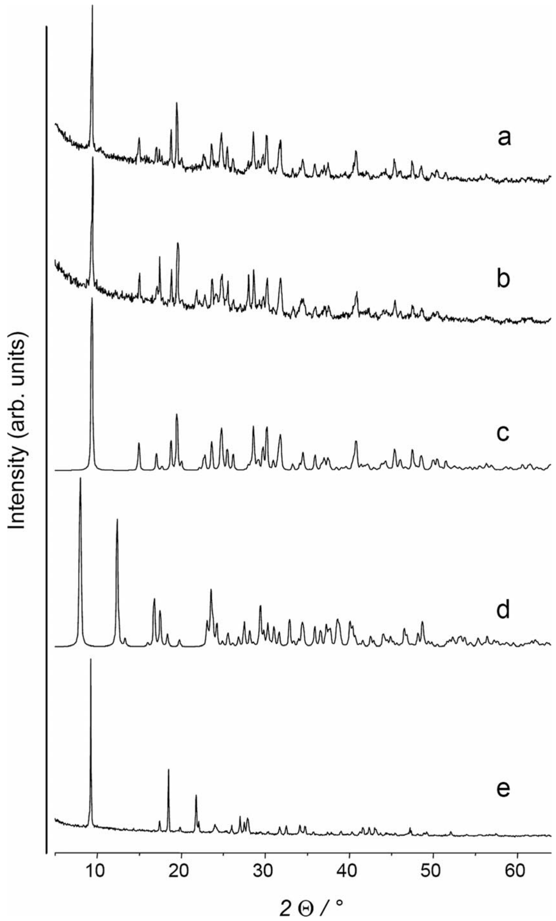


Figure 6. X-ray powder diffractograms of the products obtained by milling of (a) $Ba(OH)_2$ with H_2BDC (molar ratio: 1:1) for 1 h, (b) $Ba(OH)_2\cdot H_2O$ with terephthalic acid (molar ratio: 1:1) for 4 h, (c) powder diffractogram of $Ba(C_8H_4O_4)$, recalculated from single crystal data,[4] (d) powder diffractogram of $Ba(C_8H_4O_4)\cdot 4H_2O$, calculated from own single crystal structure data, (e) $Ba(OH)_2\cdot 8H_2O$ with H_2BDC (molar ratio: 1:1) for 4 h.

Milling experiments (milling time: 4 h, molar ratio: 1:1) using $Ba(OH)_2\cdot 8H_2O$ and terephtalic acid as precursors resulted in a sample with a completely new powder pattern (Figure 6e), not identical with that of $Ba(C_8H_4O_4)$ (Figure 6a–c) and also not in agreement with the powder pattern of $Ba(C_8H_4O_4)\cdot 4H_2O$, recalculated from own and literature single crystal data[2] (Figure 6d). The same new powder pattern (Figure 6e), but with a worse signal to noise ratio (worse crystallinity) and slightly changed relative intensities of the reflections, is obtained with shorter milling times (1 h, not shown here). On the other hand, longer milling times, here 8 h, lead to a further removal of water, and, as a consequence, the new product decomposes. The final powder pattern indicates the formation of $Ba(C_8H_4O_4)$, i.e., the water-free terephthalate.

The thermal behavior of the new product (Figure 6e) is given in Figure 7. The total mass loss of 8.2 % up to 400 °C does not correspond to a trihydrate, where a loss of about 15 % should be expected. Moreover, for a tetrahydrate, known from the literature,[2] the mass loss should be with 19.3 % even higher. However, an assumed sum formula of $Ba(C_8H_4O_4)\cdot 1.5H_2O$ exactly fits to this mass loss, and also $Ba(C_8H_4O_4)\cdot$

$2H_2O$, with a mass loss of 10.7 % at water release, is nearby. The same intermediate result is obtained with elemental analysis (Table S1). Bearing in mind that the carbon content is usually found a bit too low, the values obtained by thermal and elemental analysis along with the powder pattern (Figure 6e) can be allocated either to $Ba(C_8H_4O_4)\cdot 2H_2O$ or to $Ba(C_8H_4O_4)\cdot 1.5H_2O$.

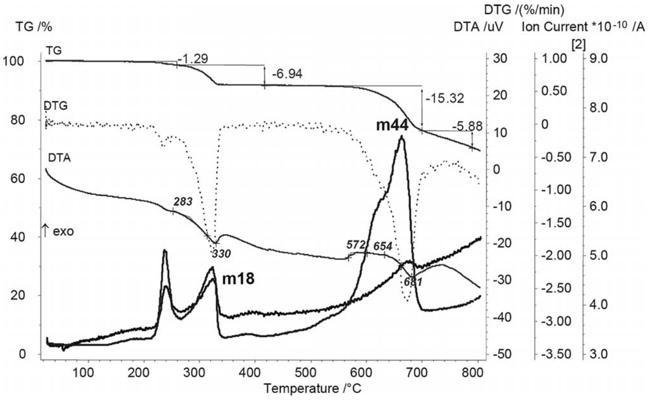


Figure 7. Thermoanalytical curves of the new product prepared by milling $Ba(C_8H_4O_4)\cdot 8H_2O$ with H_2BDC (molar ratio: 1:1) for 4 h; (m18: H_2O, m44: CO_2).

Attempts to grow single crystals from the new milling product were successful. However, their structure can be unambiguously identified as $Ba(C_8H_4O_4)\cdot 4H_2O$ in agreement with the crystal structure database.[2] The calculated powder pattern (Figure 6d) shows that the formed single crystal does not correspond to the powder sample obtained originally by milling (Figure 6e).

All ^1H-^{13}C CP MAS spectra of the products obtained from mechanochemical reactions of $Ba(OH)_2$, $Ba(OH)_2\cdot H_2O$, and $Ba(OH)_2\cdot 8H_2O$ with H_2BDC are summarized in Figure 8. In agreement with XRD patterns these spectra are identical for the samples obtained by mechanochemical reactions with $Ba(OH)_2$ and $Ba(OH)_2\cdot H_2O$ (Figure 8a, b) and are the typical signals of $Ba(C_8H_4O_4)$. Carbon resonances of the third product (Figure 8c) are different and indicate the formation of a new $Ba(C_8H_4O_4)\cdot nH_2O$, which is assumed to be $Ba(C_8H_4O_4)\cdot 2(1.5)H_2O$.

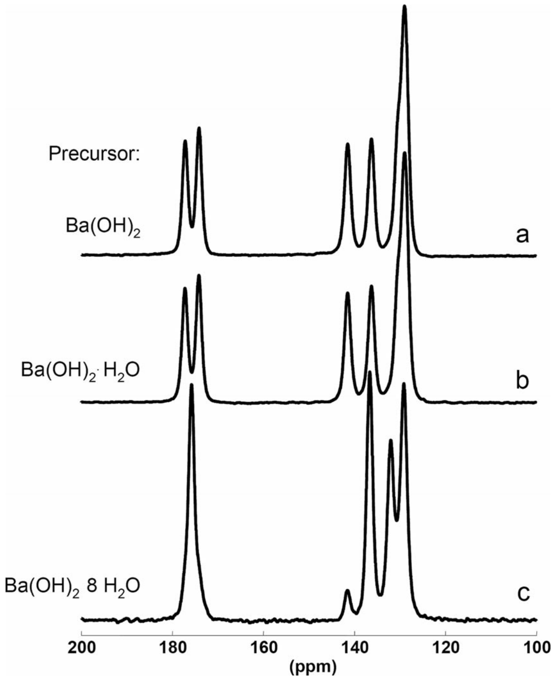


Figure 8. ^1H-^{13}C CP MAS NMR spectra of samples prepared by milling of: (a) $Ba(OH)_2$ with H_2BDC (molar ratio: 1:1) for 1 h, (b) $Ba(C_8H_4O_4)\cdot H_2O$ with H_2BDC (molar ratio: 1:1) for 4 h, (c) $Ba(C_8H_4O_4)\cdot 8H_2O$ with H_2BDC (molar ratio: 1:1) for 4 h (ν_{rot} = 10 kHz, p15 = 6 ms).

Conclusions

With the presented study we have shown that a mechanochemical synthesis of alkaline earth metal terephthalates $M(C_8H_4O_4)\cdot nH_2O$ (M = Ca, Sr, Ba) is in general possible. A successful mechanochemical reaction depends on the cation, the water supply of the precursor compounds, and the milling impact.

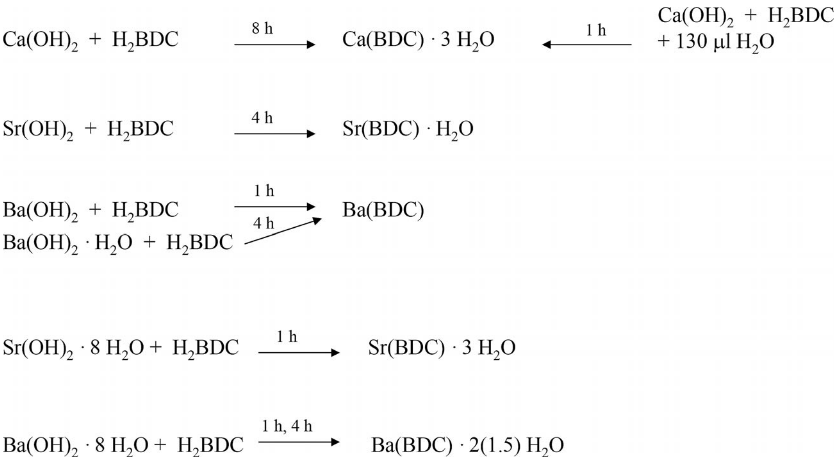
In general, the necessary milling time decreases with increasing cationic radius. Thus, 8 h of milling are necessary for the synthesis of $Ca(C_8H_4O_4)\cdot 3H_2O$ from $Ca(OH)_2$ and terephthalic acid, and, the crystallinity of the product is bad. This situation can be distinctly improved after the addition of only few microliters of water to the mixture of precursor compounds. With liquid assisted grinding the milling time can be considerably reduced to only 1 h and phase pure $Ca(C_8H_4O_4)\cdot 3H_2O$ is obtained. A thermal post-treatment of the trihydrate results in $Ca(C_8H_4O_4)$.

In addition to the mechanochemical synthesis described for $Sr(C_8H_4O_4)\cdot 3H_2O$ in Ref. [5] with $Sr(OH)_2\cdot 8H_2O$ as starting material, a successful mechanochemical formation of $Sr(C_8H_4O_4)\cdot H_2O$ is possible starting from $Sr(OH)_2$ and terephthalic acid in a molar ratio 1:1. The use of the water free hydroxide requires a stronger mechanical impact (4 h of milling) for a successful reaction. Recrystallization experiments resulted in $Sr(C_8H_4O_4)\cdot 4H_2O$ and showed that $Sr(C_8H_4O_4)\cdot 3H_2O$ is only accessible on the mechanochemical route.

The mechanochemical synthesis of $Ba(C_8H_4O_4)$ is very easy both with $Ba(OH)_2$ and $Ba(OH)_2\cdot H_2O$ as starting materials. Starting with $Ba(OH)_2\cdot 8H_2O$ at milling the formation of a new barium terephthalate hydrate, so far identified as $Ba(C_8H_4O_4)\cdot 2(1.5)H_2O$, can be reported.

Also in the barium system, the single crystals obtained after recrystallization, possess a structure and composition different from the powder obtained after milling. It seems that chemical reactions induced in a planetary mill open a way to new compounds not accessible by classical solution chemistry.

The simplified reaction paths for the successful mechanochemical formation of alkaline earth metal terephthalates are summarized in Scheme 1. Further milling experiments with organic linkers different from terephthalic acid are in progress.



Scheme 1. Reaction paths for the formation of $M(C_8H_4O_4)\cdot nH_2O$. Time on the arrows indicates the respective milling time (see Experimental Section).

Experimental Section

Preparation: All mechanochemical reactions were performed in a commercial planetary mill "Pulverisette 7 premium line" (Fritsch, Germany) under access of air. Each silicon nitride grinding bowl was filled with 1 g of a powder mixture and assembled with five silicon nitride balls. A ball to powder mass ratio of 14.5 was ensured. All samples were milled with a rotational speed of 600 rpm and different milling times, mentioned in the text.

Commercially accessible powders of $Ca(OH)_2$, $Sr(OH)_2$, $Sr(OH)_2\cdot 8H_2O$, $Ba(OH)_2$, $Ba(OH)_2\cdot H_2O$, and $Ba(OH)_2\cdot 8H_2O$ were used as alkaline earth metal sources. They were milled with terephthalic acid [1,4-$(COOH)_2$–C_6H_4, (H_2BDC), Aldrich, chemical purity 98 %] in a molar ratio of 1:1 if not otherwise indicated.

In addition, simple attempts by grinding the two precursors together in a mortar were done.

The products obtained by milling $Sr(OH)_2\cdot 8H_2O$ [or $Ba(OH)_2\cdot 8H_2O$] with H_2BDC (1:1) were recrystallized from water and cubic colorless crystals were formed. This was done by adding about 3 mL of water to a small amount (one small spatula) of the product, shaking with hand, and waiting until two different layers (aqueous and non aqueous) were formed. Some white particles precipitated down. The two layers were removed by a glass pipette into a new vial. Almost 7–10 d later the crystals were formed.

XRD: X-ray diffractograms were recorded with a XRD-3003-TT diffractometer (Seiffert & Co., Freiberg) with Cu-K_α radiation (λ = 1.542 Å; 2 θ range: $5° \leq 2\ \theta \leq 64°$; step scan: 0.05°, step time: 5 s). Reflections were compared with diffractograms of the JCPDS-PDF data base.[12]

MAS NMR Spectroscopy: ^1H-^{13}C CP MAS NMR spectra were recorded with a Bruker AVANCE 400 spectrometer (Larmor frequency: ν_{13C} = 100.6 MHz) with a 4 mm MAS probe (Bruker Biospin). ^{13}C chemical shift values are given with respect to TMS. All ^1H-^{13}C CP MAS NMR spectra were taken with different contact times (p15) ranging from 200 µs to 8.5 ms.

Thermal Analysis: The thermal behavior was studied with a NETZSCH thermoanalyzer STA 409 C *Skimmer*®, being additionally equipped with a conventional high-temperature SiC oven. A DTA-TG sample carrier system with platinum crucibles (baker, 0.8 mL) and Pt/PtRh10 thermocouples were used. Measurements were performed in a nitrogen atmosphere applying a heating rate of 10 $K\cdot min^{-1}$.

Elemental Analysis: Carbon, nitrogen, and hydrogen contents were determined with an EURO EA equipment (HEKAtech GmbH).

FT IR: IR spectra were recorded in transmission in the range of 4000–750 cm^{-1} using KBr pellets. The spectrometer system was a Perkin-Elmer FT-PE Spectrum System 2000.

Supporting Information (see footnote on the first page of this article): FT-IR- and MAS NMR spectra, thermoanalytical curves and results of the elemental analyses for the samples under consideration.

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