Mechanochemistry of fluoride solids: from mechanical activation to mechanically stimulated synthesis

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Abstract
This lecture text is focused on the comparatively young field of mechanochemistry of fluoride solids, considering both their mechanical activation and their mechanochemical synthesis. Beside a literature survey, the mechanochemical synthesis of binary fluorides MF₂, MF₃, of complex fluorides MMgF₄, of solid solutions Mₙ⁺Mₚ⁻ₓF₂ or M₁₋ₓLnₓF₂₊ₓ (Ln: Y, Eu) and of fluorine-containing coordination polymers is presented. Owing to their interesting potential applications in the field of fluoride ion conductivity or luminescence properties when doped, most of the given examples are alkaline earth metal compounds. A short historical survey, remarks on peculiarities and consequences of mechanical activation as well as the necessary technical equipment for mechanochemical reactions precede the section.

Graphic abstract

Keywords Mechanical activation · Mechanochemical synthesis · Solid fluorides

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Introduction

Mechanochemistry is still not sufficiently present in chemistry textbooks. Therefore, it is hoped that this text will fill the gap.

Mechanically induced reactions have been known and used for thousands of years. Therefore, it is really surprising that mechanochemistry is both one of the less understood and one of the less studied fields of chemistry. Nevertheless a tremendous number of mechanochemical syntheses were successfully performed since the beginning of the twenty-first century. Mechanochemical syntheses are for instance applicable to prepare inorganic and organic materials, co-crystals, intermetallic compounds, nanomaterials, active pharmaceutical ingredients or inorganic–organic hybrid materials. A comprehensive recent survey of applications of mechanochemistry is given by Baláž et al. [1]. The general possibility of mechanochemical syntheses is therefore related to all imaginable local bonding situations in solids, i.e. mechanically induced rupture and formation of covalent, ionic or metallic bonds along with the influence of mechanical forces on weak intra- and intermolecular interactions like hydrogen bridges.

Mechanically induced solid-state chemical reactions can be performed completely without solvents. Ideally, by-products disappear via the gaseous phase. As a consequence, solid-state mechanochemistry is an attractive alternative to classical, solvent-based syntheses routes and can be regarded as green chemistry. Moreover, metastable products or phases can be obtained which are not accessible using other synthesis strategies.

Ball milling techniques without additional solvents are widely used in mechanochemistry. Altogether one can observe the following phenomena involved in milling: on the one hand, a dramatic reduction of the particle sizes occurs, dependent on the milling tools down to the nanometre range and a possible amorphization of the starting materials. On the other hand, new compounds with good crystallinity can be built up during milling, and in addition, their crystallinity can be even improved with ongoing mechanical impact.

Mechanochemistry opens numerous potential applications of as-prepared materials. Therefore, the present contribution introduces first of all peculiarities of mechanochemical reactions and their consequences along with the necessary equipment, beside a short historical overview of the development of mechanochemistry at the beginning. Thereafter, examples of mechanical activation and mechanochemical syntheses of fluoride solids, especially of alkaline earth metal fluorides and fluorine-containing coordination polymers, are the focus of this publication.

The interest on binary fluorides and nanostructured solid solutions of fluorides with fluorite structure, especially alkaline earth metal fluorides, increased substantially during recent years. Two fundamental properties of these substances are responsible for this trend:

(i) Their fluoride ion conductivity, making them suitable as electrolyte materials for fluoride ion batteries or fluoride ion conductors in chemical sensors.

(ii) Their excellent luminescence properties in the case of doping with rare earth elements. The large band gap of fluorides and their optical transparency over a wide range are a big advantage for doping with rare earth ions. These properties allow innovative applications in displays, fluorescent ceramics, solar cells up to biological systems.

Short historical survey

Using traditional tools, i.e. a mortar and pestle, milling can be regarded as the first engineering technology starting as long ago as in the Stone Age. It was apparent very early on that much more happens than only obvious grinding and comminution processes. One of the very early “applications” is the generation of fire by friction. The oldest known document directly related to chemistry was written by Theophrastus of Eresos, a scholar of Aristotle, in 315 BCE [2]. The comminution of cinnabar (mercury sulfide, HgS) in a copper mortar led to the formation of mercury (Hg), i.e. to the reduction of mercury cations by copper metal. However, only at the end of the nineteenth century, i.e. about 2000 years later, were systematic investigations published on chemical reactions initiated by mechanical energy.

On the basis of his systematic studies on mechanically induced decomposition reactions of silver halides and mercury halides, Matthew Carey Lea (1823–1897) is regarded today as the founder of mechanochemistry [2–5] (Fig. 1). Lea found that mechanically induced chemical reactions can result in different products than thermally induced chemical reactions, a situation which was confirmed later for many reactions.

Despite these encouraging developments, publications concerning mechanochemistry were rare in the first half of the twentieth century. At this point, however, one has to mention the important merit of Wilhelm Ostwald (1853–1932, Fig. 1), who introduced for the first time the general term mechanochemistry into the systematics of chemistry [6]. Only in the 1960s did mechanochemistry experience a considerable revival. Different groups began to work in this field, especially in the Soviet Union, in Eastern Europe.

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1 The present article is a revised and extended version of the paper published in German on occasion of the 90th birthday of Prof. Dr. Lothar Kolditz in Leibniz Online 37 (2019), the journal of the Leibniz Soziätät der Wissenschaften zu Berlin e.V. (ISBN 1863-3285).
and in the GDR. The development of mechanochemistry in this period is associated with well-known scientists like Boldyrev and Avvakumov (Novosibirsk), Butyagin (Moscow) and Zhurkow (Leningrad), in the GDR with Thiessen and Heinicke (Berlin), in Czechoslovakia with Tkácova and Baláž (Košice), in Hungary with Juhász and in Japan with Kubo and Senna [2].

In this period the scientific questions were mainly focused on the mechanical activation and mechanochemical reactions of inorganic solids, i.e. reactions of oxides, silicates as well as the processing and handling of ores. The field of mechanical alloying developed independently of this direction. These developments, occurring almost in parallel, were brought together with the foundation of the International Mechanochemical Association in 1984. The latter initiated the International Conference on Mechanochemistry and Mechanical Alloying (INCOME), which took place in 1993 for the first time in Košice and every 3 years thereafter; the last one occurred in 2017 again in Košice.

Central questions on these conferences were and are questions on mechanical and mechanochemical alloying, the processing of ores, the synthesis of complex oxides (ceramics, dielectrics) and other inorganic materials, the synthesis of pharmaceuticals, but also questions of hydrogen storage and batteries\(^2\). With the last INCOME conference in 2017 it became obvious that mechanochemistry developed enormously also in other chemical fields since the beginning of the 1990s. Meanwhile, this field of chemistry is also represented by several research groups in Western Europe and in the USA [7].

Nowadays, mechanochemistry is—beside inorganic materials—present in nearly all research areas of chemistry. These areas range from polymer chemistry, the formation of inorganic–organic hybrid materials, zeolites and metal–organic frameworks, from pharmaceutically relevant organic compounds, co-crystals, fullerenes, the field of heterogeneous catalysis, mechanochemical reactions with gaseous reactants [8], organo-metal complexes, metal-catalysed organic reactions, up to solvent-free mechanochemical reactions in organic chemistry (see also [1] and references therein). In a special issue of *Chemical Society Reviews* [9] review articles have been published representing nearly all fields of mechanochemistry, which show the aforementioned development. Still not present in that special issue was the younger field of mechanochemistry of fluoride solids, which is the focus of the present contribution.

So: what is mechanochemistry? Until now this term introduced by Ostwald in 1919 and the definition given by Heinicke in 1984 [10] are still valid: It is a field of chemistry dealing with chemical and physicochemical changes of substances in all states of matter, due to the influence and action of mechanical energy.

The present contribution is exclusively attributed to substances in the solid state, to solids, which are usually used as powders for mechanochemical reactions. At this point I recommend to read in addition the lecture text by Senna [11], who introduced the reader (i) to the basics of solid-state chemical reactions, (ii) to the role of defects and diffusion in solids for their reactivity and (iii) who compared changes in solids due to heating in comparison with milling processes.

Mechanical energy can be applied in different ways. Milling is one common option, but also the application of pressure or sonication (ultrasound) [12] is possible. All kinds of mechanical energy lead to peculiarities on and in the solids and to implications for occurring chemical reactions.

**Peculiarities and consequences of mechanical activation**

Grinding of solids diminishes the particle size. Dependent on the milling tools and the applied energy, it is possible to reduce the particle size down to the nanometer range. Starting from a phase pure solid as the material to be ground a mechanical activation occurs. What happens? The milling process has consequences on the long- and short-range order

\(^2\) Detailed information about the history of mechanochemistry is given in [2–5] including references therein.
of the material and ends up with a mechanically distorted solid material. Dependent on the starting material the distortion can lead to a complete loss of the lattice periodicity with the solid material being X-ray amorphous after milling. Such a situation can frequently be observed in the case of oxides. Emissions of photons, electrons as well as lattice components were directly proven during the mechanical activation of inorganic materials like oxides. Static charges and electrostatic discharges were observed as well as local warming [10, 13]. As result of a mechanical treatment, especially using high-energy ball mills, materials with changed chemical and physical properties are obtained. Improved catalytic activities, increased solubilities, a changed sorption behaviour up to changed chemical reaction pathways have been observed. The application of mechanical energy allows new chemical reaction pathways, which are limited by diffusion processes in solid-state chemistry induced classically by thermal energy. Different, new materials or even metastable compounds are accessible. The treatment of silver chloride is a classical example. A thermal treatment initiates melting and evaporation of silver chloride. The result of the mechanical treatment, however, is the formation of metallic silver particles and chlorine gas [4]. The latter reaction, which was the subject of research by Carey Lea [2–4], can be used nowadays to produce silver nanoparticles with high-energy mills.

Many examples exist for the changed kinetic and thermodynamic behaviour of mechanically activated materials. This situation implies numerous questions regarding the mechanism of mechanochemically initiated solid-state reactions, which is still by far not completely understood. Moreover, one can surely say that only a singular mechanism of mechanochemical reactions will not exist. The reason is provided by very different bonding situations in the mechanochemically treated materials, which demand different milling conditions.

Nevertheless, the magma-plasma model [10, 14] should be mentioned, which was the first model in mechanochemistry. It was developed in the 1960s, especially for hard and brittle inorganic materials. According to this model a large amount of energy is released on the contact area of the colliding particles, finally responsible for the formation of plasma-like states. This assumption was proven by the emission of highly excited fragments of the solid substance, by the emission of photons and electrons on an extremely short timescale [3, 10, 14]. The surface on the contact point of solid grains is highly disordered and local temperatures up to 10,000 K can be achieved. In this concept numerous excitation processes, characterized by different relaxation times, are important [3, 13]. Further models and attempts exist to explain the mechanistic aspects of mechanochemical reactions. All of them are presented in the monograph of Baláž [3], including their references for further reading.

Most of them were developed towards the end of the twentieth century.

**Technical equipment for mechanochemical reactions**

Since the majority of mechanochemical reactions is performed by milling the reactants, only milling tools are considered in this present contribution. A lot of different milling tools exist, which can be used for mechanical activation or mechanochemical reactions. A very simple one is a mortar and pestle. Simple mortar mills, vibrations mills, ball mills or planetary mills are used along with pinned disk mills or attritors (stirred ball mills) [3, 10]. Which mill is finally used depends both on the material to be studied and the necessary energy input.

For academic purposes, in the research laboratory, simple vibration mills (Fig. 2a) are usually sufficient for many chemical reactions, especially in the field of organic chemistry. In addition, planetary ball mills (Fig. 2b) are a widely used standard for high-energy ball milling. Two kinds of mills are shown as examples in Fig. 2 which are typically used in the laboratory (see also websites of companies Fritsch and Retsch3). Moreover, the most simple mechanical device, a mortar and pestle, is shown in Fig. 2c for completeness.

The milling tool of the vibration mill (Fig. 2a) consists of two hemispheres and usually one to two milling balls of the same material. The material to be ground is placed in the hollow sphere. After fixing the cover the vibrations occur vertically, in most cases with a frequency of 50 Hz. Very often the milling tool is made of stainless steel. But polymer materials were also successfully used, because they additionally allow an in situ coupling to modern analytical methods (e.g. Ref. [15]). The grinding beakers of a planetary mill are rotatable mounted on a base plate (Fig. 2b). Base plate and milling beaker move contrarily, giving the mill therefore the name planetary mill (cf. Fig. 2b, with the mill Pulverisette 7, Fritsch company, as prototype of a planetary mill). As a result of the high-energy impact, milling beakers and balls are manufactured from hard, abrasion-resistant materials like silicon nitride, zirconium oxide, corundum, tungsten carbide or hardened steel.

**Mechanochemistry of fluoride solids**

Studies on mechanochemistry of fluoride solids started with few exceptions comparatively late, only in the beginning of the twenty-first century. Investigations on the synthesis of

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3 https://www.fritsch.de/probenaufbereitung/mahlen/; https://www.retsch.de/de/produkte/.
(i) ternary fluorides $\text{AZnF}_3$ (A: K, Na, NH$_4$) with perovskite structure [16], (ii) complex fluorides $\text{ARF}_4$ (A: alkaline metal cations, R: rare earth element cations) [17] or (iii) of lanthanum oxide fluoride LaOF from LaF$_3$ and La$_2$O$_3$ [18] have to be mentioned. All of them were focused on the excellent optical properties of the materials as one possible application. On the other hand, inorganic fluorides are known as fluoride ion conductors, a property which can be explored in electrochemical devices or batteries. The small size and the single negative charge allow a fast movement of fluoride ions in solids.

Staring from crystalline SnF$_2$ and PbF$_2$, both are well known as very good fluoride ion conductors, ternary and quaternary fluorides have been mechanochemically synthesized [19–21]. The systems MF$_2$–SnF$_2$ (MSnF$_4$, M: Pb, Ba) are the fastest fluoride ion conductors known nowadays [22–24]. This high conductivity can be in addition considerably increased by the mechanochemical synthesis. Structural disorder in the grain surfaces, small particle sizes, introduced defects and short diffusion paths are responsible for this additional effect [25–28]. For example, the high electric conductivity of PbSnF$_4$ is shown in Fig. 3 as a function of the temperature. Higher temperature (lower $T^{-1}$ values) results in a strong increase of the electric conductivity. Finally, solid solutions of the general composition Pb$_{1-x}$Sn$_x$F$_2$ have also been mechanochemically synthesized [29, 30].

However, mechanochemical syntheses were not only restricted to the albeit promising chemical system PbF$_2$–SnF$_2$. Thanks to the successful activities of the research groups of Heitjans (Leibniz University Hannover, Germany) and Wilkening (University Graz, Austria) the number of mechano-synthesized fluorides was remarkably expanded. Ion dynamics in these new solids was substantially studied by solid-state NMR and impedance spectroscopy, respectively.

The mechanochemical synthesis of fluorides with inverse perovskite structure like BaLiF$_3$ [31–34] or (Ba,Sr)LiF$_3$ [35, 36] was very successful. The mutual substitution of Ba$^{2+}$ with Sr$^{2+}$ ions was impressively demonstrated using high-speed $^{19}$F magic angle spinning (MAS) NMR spectra (Fig. 4), which allowed the distinct discrimination between the five possible local structure units around fluorine.

Furthermore, the successful mechanochemical synthesis of the following complex fluorides has been reported: BaMgF$_4$ [37, 38], SrMgF$_4$ [39], BaSn$_2$F$_5$ [40], RbSn$_2$F$_5$ [41], NaSn$_2$F$_5$ [42], KSn$_2$F$_5$ [43] and Li$_3$AlF$_6$ [44]. Moreover, the mechanochemical synthesis was successful for solid solutions of (i) alkaline earth metal fluorides or PbF$_2$ with cubic symmetry M$^{1+}$,M$^{2+}$F$_2$ (M: Ca, Sr, Ba, Pb) (fluorite structure) [45–49], of (ii) alkaline earth metal fluorides with rare earth fluorides or YF$_3$ [50–54] or of (iii) SnF$_2$ with alkaline metal fluorides [55, 56].
The authors were able to show that the mechanochemical route, partially combined with thermal post-treatment, is a simple synthesis method for nanocrystalline fluoride solids [57, 58]. All of the mentioned compounds are fast fluoride ion conductors after mechanical treatment. Preishuber-Pflügl and Wilkening gave a nice overview of local structures and ion dynamics in such defect-rich fluorides listed earlier [38]. Moreover, Patro very recently published an overview of the influence of milling process variables in a planetary mill on the synthesis and ion transport properties of fast fluoride ion conductors [59].

All syntheses mentioned above started from commercially available binary crystalline fluorides $MF_2$, $MF$ or $MF_3$. Dependent on the desired final composition, their molar ratios were adjusted and their mixed fluoride powders were added into the grinding beakers, usually under dry conditions. Thus, a milling of solid fluorides was performed, which makes a serious mechanical impact necessary resulting finally in many hours of high-energy ball milling.

**Mechanical activation**

Beside the mechanically induced synthesis of aforementioned solid solutions or complex fluorides, only a few publications exist which focused on milling of pure crystalline fluorides and the effects on their structure and properties. Known are milling experiments with $BaF_2$ [60], $SnF_2$, $CaF_2$ [47, 48] and $AlF_3$. Patro et al. were able to show that milling time, while keeping all other milling conditions unchanged, has a significant effect on crystallite sizes and micro-strains of $SnF_2$ particles [21]. Impedance measurements demonstrated that the DC conductivity is reciprocally proportional to the crystallite size. It means that both properties can be adjusted using ball milling techniques.

The influence of high-energy ball milling on crystalline $CaF_2$ was studied in our group [61] and also later by Abdellatif et al. [62]. The main analytical techniques used were X-ray powder diffraction, $^{19}$F solid-state NMR, but also transmission electron microscopy (TEM). One important result, especially in comparison with oxide compounds, is a missing detectable amorphization of the fluoride powder samples after milling. And if all, it can then only be found at the grain boundaries of the small particles. Only nanocrystalline $CaF_2$ particles are obtained by applying even strongest mechanical impacts. Beside a broadening of the X-ray reflections and $^{19}$F resonances, the spin lattice relaxation time $T_1$ of the $^{19}$F nuclei gives a sensitive indication for the influence of the mechanical impact [61, 62]. While for the commercial crystalline $CaF_2$ a $T_1$ time ($^{19}$F) of 91.2 s was determined, 4 h of milling in a planetary ball mill decrease this time to 3.9 s [61]. Moreover, increased fluoride ion conductivities were achieved using $CaF_2$ samples with enhanced surface defect structures obtained by the application of vapour pressure followed by high-energy ball milling [63, 64].

A similar effect, i.e. the formation of nanocrystalline particles, was observed on the mechanical activation of $\alpha-AlF_3$, the stable rhombohedral phase of aluminium fluoride [65] as well. The $^{19}$F spin lattice relaxation time was reduced from 175.8 s (crystalline starting material) to 5.4 s for the nanocrystalline sample after 16 h of milling.

Obviously, here the comminution of crystallites is also the dominant process during milling. In addition, the mechanical impact generates both Bronsted and Lewis acid sites on the surface of aluminium fluoride. In contrast to the crystalline starting material, the nanocrystalline $\alpha-AlF_3$ sample prepared by milling is catalytically active. This was proven by the dismutation reaction of $CHClF_2$. In addition, the proportion of Bronsted and Lewis acid sites can be adjusted by the chosen atmosphere during milling. Dry milling produces mainly Lewis acid sites, whereas air milling results in both Bronsted and Lewis acid sites [65].

Another powerful and flexible approach to obtain nanoscaled metal fluorides is the fluorolytic sol–gel synthesis, which was comprehensively documented in the lecture text by Kemnitz et al. ([66] and references therein).
Mechanochemical synthesis: fluorination in the mill

The mechanochemical synthesis of solid fluorides, solid solutions of fluorides or complex fluorides with distinguished properties starting from powders is in general possible along two different reaction pathways:

The first way was followed in all publications cited above. The mechanochemical synthesis was carried out using different binary fluorides $MF_n$ as reactants, i.e. all used reactants were already fluorine compounds. The second possible pathway was discovered and then followed systematically in our group at Humboldt-Universität zu Berlin.

The general reaction principle of all examples mentioned hereinafter is the fluorination of fluorine-free metal compounds $MX_n$ like metal acetates, carbonates, hydroxides or alkoxides by milling with ammonium fluoride ($\text{NH}_4\text{F}$) directly in the planetary mill. It means that both the fluorination and the chemical reaction take place only under the influence of a mechanical impact [see, for example, also Eq. (1)].

During the mechanochemical synthesis of coordination polymers, perfluorinated organic compounds were used exclusively in addition to ammonium fluoride as fluorinating agent.

First of all, however, the idea of fluorination of fluorine-free reactants in the mill was followed to synthesize binary fluorides themselves in a mechanochemical way.

**Binary fluorides: $MF_2$**

After a first attempt to synthesize $CaF_2$ using $CaCO_3$ and $\text{NH}_4\text{F}$ as reactants [61], the general possibility of a mechanochemical synthesis of binary fluorides was published in 2012 for the first time [67]. The reaction according to Eq. (1) provides an easy, fast, direct and solvent-free access to nanocrystalline alkaline earth metal fluorides $MF_2$.

$$MX_2 + 2\text{NH}_4\text{F} \rightarrow MF_2 + 2\text{NH}_3 + 2\text{HX}$$  \hspace{1cm} (1)

For alkaline earth metal fluorides crystallizing in fluorite-structure (M: Ca, Sr, Ba) the synthesis according to Eq. (1) is possible, almost independent of the kind of the fluorine-free reactant [67]. All formed by-products leave the mill via the gaseous phase. The as-prepared alkaline earth metal fluorides are nanocrystalline and phase pure. For example, the X-ray powder diffractograms of mechanochemically synthesized $BaF_2$ [according to Eq. (1)] are shown in Fig. 5.

For magnesium fluoride this situation is different. The following magnesium compounds were tested as starting materials: $\text{Mg(OH)}_2$, $\text{MgO}$, $\text{Mg(CH}_3\text{COO})_2$, $\text{Mg(CH}_3\text{COO)}_2\cdot\text{H}_2\text{O}$, $\text{Mg(CH}_3\text{COO)}_2\cdot4\text{H}_2\text{O}$, $\text{Mg(OH)}_2(\text{CO}_3)_4\cdot4\text{H}_2\text{O}$ and $\text{Mg(CH}_3\text{CH}_2\text{O})_2$. However, only in the case of $\text{Mg(CH}_3\text{COO)}_2\cdot4\text{H}_2\text{O}$ as reactant can $\text{MgF}_2$ (crystallizing with rutile structure) be synthesized in this way, though not phase pure.

This mechanochemical synthesis can be further simplified using alkaline earth metal hydroxides or hydroxide hydrates as reactants, which holds for $Ca^{2+}$, $Sr^{2+}$ and $Ba^{2+}$ as metal cations. De facto, a mechanical impact is here no longer necessary with these reactants. Simply shaking the two solid powdered reactants for 30 s is sufficient (cf. Eq. (1), [67], see also Fig. 5b and the illustration given in Fig. 6). Later we were able to show that even simple mixing with a spatula works [68].

The contact of hydroxyl groups (water) with ammonium fluoride leads presumably to additional local formation of HF, which might accelerate the fluorination of the starting material. Such as-prepared nanocrystalline samples possess fluoride ion conductivities, which are astonishing high and distinctly higher than those of comparable microcrystalline samples [68].

Also lead fluoride $\text{PbF}_2$ can be mechanochemically synthesized according to Eq. (1) [69]. Here, the choice of the fluorine-free precursor compound is decisive for the $\text{PbF}_2$ phase finally formed. The usage of lead oxide $\text{PbO}$ results in the orthorhombic $\alpha$-$\text{PbF}_2$ phase, whereas the usage of lead acetate $\text{Pb(CH}_3\text{COO})_2$ results in the cubic $\beta$-$\text{PbF}_2$ phase (fluorite structure). Starting with lead carbonate results in a mixture of both phases [69] (see also Fig. 7).

A similar chemical pathway was followed by Subirana Manzanares et al. [70]. The starting samples $\text{Pb(CH}_3\text{COO)}_2\cdot3\text{H}_2\text{O}$ and $\text{NH}_4\text{F}$ were ground in a mortar and organic additives, e.g. citric acid or amines, controlled the formation of the orthorhombic and the cubic phase of $\text{PbF}_2$, respectively. Here, the use of amines favours the formation of the orthorhombic phase of $\text{PbF}_2$ [70].

All in all it is worth mentioning that all mechanochemical reactions were performed under normal conditions. An increased humidity or an increased content of crystal water in the reactants had a positive effect on the formation of binary fluorides $MF_2$.

**Binary fluorides: $MF_3$ ($\text{AlF}_3$, $\text{GaF}_3$)**

Unfortunately, it was not possible to transfer the successful mechanochemical synthesis principle of alkaline earth metal fluorides (Eq. 1) to the formation of earth metal fluorides.
Extensive studies to synthesize aluminium fluoride according to Eq. (1) led, independent of the starting material (Al(OiPr)$_3$, AlOOH, Al(CH$_3$COO)$_2$OH), always to the same result: the thermodynamically stable ammonium hexafluoroaluminate ((NH$_4$)$_3$AlF$_6$) is formed as long as NH$_4^+$ ions are available during the chemical reaction [71], Eq. (2) (Fig. 8).

Substitution of NH$_4$F by e.g. NaF results in remaining Na$^+$ ions in the matrix. And in this special combination the formation of cryolite (Na$_3$AlF$_6$) or chiolite (Na$_5$Al$_3$F$_{14}$), i.e. the formation of complex fluorides, can be observed [73, 74].

Similar to Eq. (2) Lu et al. [72] mechanochemically synthesized ammonium hexafluorgallate, (NH$_4$)$_3$GaF$_6$, starting from GaF$_3$·3H$_2$O and NH$_4$F. However, the authors were not able to prepare gallium fluoride (GaF$_3$).

Consequently, the formation of binary fluorides MF$_3$ would require another fluorinating agent without ammonium ions. This situation is problematic bearing in mind the requirement that additionally formed compounds should disappear via the gaseous phase.

\[
\text{AlX}_3 + 6 \text{NH}_4\text{F} \rightarrow (\text{NH}_4)_3\text{AlF}_6 + 3 \text{NH}_3 \uparrow + 3 \text{HX} \uparrow \tag{2}
\]

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$^4$ (OiPr: isopropylate).

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![Fig. 5 X-ray powder diffractograms taken after reaction of Ba(OH)$_2$·8H$_2$O with NH$_4$F (Ba/F=1:2): a after 4 h milling in the planetary mill, b after 30 s shaking, c after thermal treatment in a quasi-closed Pt crucible (Q-crucible), d after thermal treatment in an open Pt crucible. For comparison, the diffractogram of crystalline BaF$_2$ is given as reference. Reproduced from [67]. Copyright 2012 Elsevier Masson SAS. All rights reserved](image)

![Fig. 6 Illustration of the preparation of alkaline earth metal fluorides MF$_2$, simply by shaking. Reproduced from [67]. Copyright 2012 Elsevier Masson SAS. All rights reserved](image)
As already observed in the case of the formation of binary fluorides MF$_2$, the presence of humidity or an adjusted water content of the starting compounds promotes the formation of complex fluorides with different product composition. The latter was tested for the reaction of NaF with AlF$_3$ to form cryolite or chiolite (Fig. 9). It demonstrates that an adjusted degree of humidity results in different product compositions [74].

In principle, a mechanochemical synthesis of AlF$_3$ is only possible if further cations can be avoided. Surprisingly, a milling attempt using β-AlF$_3$·3H$_2$O with the aim simply to remove the crystal water and to end up with AlF$_3$ is not successful, which is in contradiction to the classical thermal treatment in a furnace using quasi-isobar crucibles. Instead, the use of β-AlF$_3$·3H$_2$O as fluorinating agent allows mechanochemical reactions with aluminium hydroxides and as a result the formation of aluminium hydroxide fluorides, AlF$_3$(OH)$_{1-x}$·$n$H$_2$O. Dependent on the respective supplied Al/F molar ratio, crystalline (Al/F < 1) or X-ray amorphous compounds (Al/F > 1) are formed [75–78].

The mechanochemical synthesis of aluminium fluoride AlF$_3$, however, is not possible.

**Complex fluorides: MF$_2$–MgF$_2$ (MMgF$_4$, M: Ca, Sr, Ba)**

The mechanochemical synthesis of BaMgF$_4$ using the binary fluorides BaF$_2$ and MgF$_2$ [37] is also possible by applying the fluorination of fluorine-free starting materials with ammonium fluoride directly in the mill (Eq. (1), [79]). Provided that the respective molar ratio of reactants is used, a direct and stable formation of tetrafluoromagnesates MMgF$_4$ depends in addition on the radius of the alkaline earth metal cation. With decreasing radius of the cation M$^{2+}$ (Ba$^{2+}$ > Sr$^{2+}$ > Ca$^{2+}$) the formation of MMgF$_4$ is more and more difficult [79]. The crystal structures of strontium- and barium tetrafluoromagnesate are shown in Fig. 10 with the same view along the a-axis.

**Solid solutions: M$_a$R$_{1-x}^+$F$_2$ (M$_b$: Ca, Sr, Ba, Pb); M$_{1-x}$Ln$_x$F$_{2+x}$ (M: Ca, Sr; Ln: Y, Eu)**

The mechanochemical synthesis of solid solutions of alkaline earth metal fluorides with fluorite structure according to Eq. (3) is very easily possible [80, 81].

\[
(1-x) \underset{a}{M} R_2 + x \underset{b}{M} R_2 + 2 \text{NH}_4 \text{F} \rightarrow \underset{\text{a}}{M}^{1-x} \underset{\text{b}}{M}^x \text{F}_2 + 2 \text{NH}_3 + 2 \text{HR} \tag{3}
\]

(R: OH$^-$, OAc$^-$, 0.5 CO$_3^{2-}$)

Equation (3) holds for those cations M$^a$ and M$^b$ which form themselves binary fluorides with fluorite structure. The mutual substitution of cations on their lattice positions was directly proven with the help of $^{19}$F solid-state NMR spectroscopy. Fluorine is tetrahedrally coordinated by four cations in the cubic fluorite structure ([FM$_4$]). Therefore, five possibilities exist for the local coordination of fluorine on the formation of solid solutions (Eq. 3): [FM$_{a-x}$M$_x^a$], with 0 ≤ $x$ ≤ 4. Exemplarily, a $^{19}$F MAS NMR spectrum of Sr$_{0.5}$Pb$_{0.5}$F$_2$ with all five possible fluorine coordinations and their respective assignments is shown in Fig. 11.

From literature data it was already known that the formation of solid solutions of different fluorides has an additional positive effect on fluoride ion conductivities. These findings were verified for solid solutions mechanochemically synthesized according to Eq. (3). The DC fluoride ion conductivities shown in Fig. 12 for the combination of cations Ba–Pb are distinctly higher than those for nanocrystalline PbF$_2$, which is known as an excellent fluoride ion conductor.
A mechanochemical fluorination with NH$_4$F according to Eq. (3) is likewise successful for a doping with rare earths [82, 83]. For a doping with Eu$^{3+}$ cations it was shown that the solvent-free mechanochemical synthesis route results in nanocrystalline fluorides with remarkably long luminescence lifetimes of the excited states of europium [83]. The latter opens additional interesting optical applications for such fluorides.

**Fluorine-containing coordination polymers of alkaline earth metals**

This overview finishes with some future prospects of ongoing research projects on the mechanochemical synthesis of fluorine-containing coordination polymers of alkaline earth metals.

In general, two principal possibilities exist for the implementation of fluorine in such compounds. Either fluorine is introduced with the perfluorinated organic compound...
(linker) (Eq. 4) or the fluorination of the reactants takes place with ammonium fluoride directly in the mill (Eq. 5).

\[
M(OH)_2 + H_2BDC-F_4 \rightarrow M(BDC-F_4):xH_2O \tag{4}
\]

\[
M(OH)_2 + 0.5H_2p-BDC + NH_4F \rightarrow MF(p-BDC)_{1.05} + NH_3 + 2H_2O \tag{5}
\]

\((H_2p-BDC-F_4\): tetrafluoroterephthalic acid (tetrafluoro-para-benzenedicarboxylic acid))

Initially it was shown that the simple mechanochemical synthesis using alkaline earth metal hydroxides and terephthalic acid \((H_2p-BDC, \text{fluorine-free})\) is possible. Ca, Sr, and Ba terephthalate hydrates were formed in this way up to partially new compounds [84, 85]. Hydroxides or hydroxide hydrates were ideal starting materials, as found before for the synthesis of binary fluorides. Moreover, a synthesis protocol was available, which can be completely transferred to the synthesis with perfluorinated linkers.

Use of different tetrafluorobenzenedicarboxylic acids with carboxylic groups in para, meta and ortho position \((H_2p-BDC-F_4, \ H_2m-BDC-F_4, \ H_2o-BDC-F_4)\) allowed numerous so far unknown coordination polymers to be mechanochemically synthesized. Structure and properties of these new compounds were comprehensively characterized. Standard analytical methods like X-ray diffraction, solid-state NMR and FTIR spectroscopies, but also methods of thermal analysis, elemental analysis, BET measurements and methods of dynamic gas absorption (DVS, dynamic vapour sorption) were employed. Structure determinations were performed from X-ray diffraction powder data, since the mechanochemical synthesis does not allow the formation of single crystals [86–92]. Figure 13 gives an insight into the structure of Ca(Sr)(p-BDC-F_4)-4H_2O, as one representative example of the numerous new compounds. Here, the alkaline earth metal cations Ca\(^{2+}\) (Sr\(^{2+}\)) possess a nine-fold oxygen coordination (Ca(Sr)O\(_9\), Fig. 13) [86].

![Fig. 11](image1.png)

**Fig. 11** Experimental (blue) and calculated (red) \(^{19}\)F MAS NMR spectrum of Sr\(_{0.5}\)Pb\(_{0.5}\)F\(_2\) along with the assignment of \(^{19}\)F resonances to the five possible local structural units [FM\(_{x}\)Pb\(_{4-x}\)]. Doublet signals are due to the visible scalar coupling \(J_{F-Pb}\). Reproduced from [81]. Copyright 2018 Elsevier Masson SAS. All rights reserved.

![Fig. 12](image2.png)

**Fig. 12** Arrhenius plot of the DC conductivities of M\(_x\)Pb\(_{1-x}\)F\(_2\) samples, prepared with different cation ratios by milling (8 h) the corresponding metal acetates with ammonium fluoride. PbF\(_2\) was prepared by milling (4 h) of Pb(OAc)\(_2\)-3H\(_2\)O with NH\(_4\)F. Reproduced from [81]. Copyright 2018 Elsevier Masson SAS. All rights reserved.
Finally, in 2018 we reported the first mechanochemical synthesis of a coordination polymer with a direct barium–fluorine bond, in BaF-benzenedicarboxylate BaF($p$BDC)$_{0.5}$ [93]. Both barium hydroxide and barium acetate can act as the barium source (Eq. 5); they are partially fluorinated by NH$_4$F if an organic linker is additionally present. Figure 14 gives a schematic overview of different reaction opportunities during milling of Ba(OH)$_2$ with organic linkers and/or NH$_4$F.

The barium terephthalate system was chosen to study the influence of different fluorine positions (fluorinated organic linker vs. direct Ba–F bond) on the lifetime of the excited states when doped with lanthanide ions (Eu$^{3+}$, Tb$^{3+}$). Here, the coordination polymer with a direct metal–fluorine bond shows the highest lifetime of the excited states of lanthanides (Eu$^{3+}$, Tb$^{3+}$ or Eu$^{3+}$/Tb$^{3+}$) [94].

Further new 2D networks with a direct metal–fluorine bond (MF(CH$_3$COO), M: Ca, Sr, Ba, Pb) were synthesized using acetates, ammonium fluoride and H$_2$p-BDC (in the case of alkaline earth metal cations) by the mechanochemical route. Crystal structures were solved from the powder data [95]. Their local structures and crystal structures are depicted in Figs. 15 and 16. The only exception is the calcium compound, which cannot be obtained phase pure. As in the cubic alkaline earth metal fluorides, fluorine is also in acetate fluorides four-fold coordinated by the cations ([95], Figs. 15, 16). A comparison of structure and properties of fluorinated and non-fluorinated Ba-coordination polymers is published in Ref. [96], comparing barium acetate fluoride, barium trifluoroacetate and barium acetate, i.e. comparing the different possibilities and consequences of fluorine integration into the networks. The fluorine position turned out to be crucial for material properties like thermal stability, vapour sorption behaviour and electrochemical performance [96].

**Conclusion**

Beside a short introduction into general and historical aspects of mechanochemistry, the present lecture text focused on the mechanochemical activation and mechanochemical syntheses of fluoride solids, especially of alkaline earth metal fluorides and fluorine-containing coordination polymers of alkaline earth metals.
The simple mechanochemical synthesis route for binary fluorides, for complex fluorides, for fluoride solid solutions and also for fluorine-containing coordination polymers shows that this solvent-free synthesis strategy can be used—via particle grinding—to build up new compounds also for these classes of inorganic materials and inorganic–organic hybrid materials, respectively. The observed interesting properties of those compounds, especially regarding fluoride ion conductivities and luminescence properties in the case of doping, combined with their easy access via mechanochemistry, are expected to result in interesting applications in the near future. For the new fluorine-containing coordination polymers of alkaline earth metals, studies of their catalytical,

Fig. 15 Local environment and crystal structure of compounds MF(CH$_3$COO) (M: Ba or Sr). a Crystal structure showing the local fluorine coordination (green polyhedra) and metal coordination sphere (blue polyhedra); b layered structure of the 2D coordination polymer (blue, metal; black, carbon; green, fluorine; red, oxygen; grey, hydrogen). Reproduced from Ref. [95] with permission from The Royal Society of Chemistry

Fig. 16 Local environment and crystal structure of compound PbF(CH$_3$COO). a Coordination around the F atom; b coordination around Pb with four oxygen atoms and four fluorine atoms; c coordination around Pb in α-PbF$_2$ for comparison; d layered 2D crystal structure with the fluorine polyhedra (green) and Pb polyhedra (blue) (grey, metal; black, carbon; green, fluorine; red, oxygen; light grey, hydrogen). Reproduced from Ref. [95] with permission from The Royal Society of Chemistry
optical, electrochemical and gas sorption behaviour are still at the beginning.

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