



An easy access to nanocrystalline alkaline earth metal fluorides – just by shaking

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ABSTRACT

High energy ball milling as fast, direct and solvent free method allows an easy access to nanocrystalline alkaline earth metal fluorides MF₂ (M: Mg, Ca, Sr, Ba). Comparable metal sources (acetates, carbonates, hydroxides, alkoxides) were used for the reaction with NH₄F as fluorinating agent. Even very simple manual shaking experiments between NH₄F and the corresponding hydroxides in the stoichiometric ratio (M:F = 1:2, M: Ca, Sr, Ba) give phase pure fluorides. Moreover, comparable classical thermal reactions in closed crucibles at higher temperatures provide phase pure crystalline fluorides in nearly all cases as well.

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1. Introduction

Alkaline earth metal fluorides attract considerable attention both as single crystals and as nanocrystalline powders. Crystals of alkaline earth metal fluorides play an important role in optics due to their wide optical band gaps ranging from the vacuum UV (<200 nm) through the infrared regions (>10 μm). Increasing interest in nanocrystalline fluoride powders is basically connected with their high anionic conductivity at higher temperatures [1]. It was shown that the fluoride ionic conductivity of nanocrystalline CaF₂ powders is orders of magnitudes larger than that of microcrystalline samples [2]. Physical phenomena like diffusion or defect mobility were extensively studied on crystalline ionic fluorides (s. e.g. [1,3,4]). Another promising direction is the preparation of optically transparent ceramics with low optical losses using fluorides as additives [5]. Moreover, alkaline earth fluorides can be used as catalysts [6,7], fluxing agents or, as in the case of nano-sized calcium fluoride, for dental applications [8]. Among them a particular role can be allocated to magnesium fluoride for the preparation of thin films [9–11], ceramic additives [12,13] or catalytic applications [7]. Bearing in mind all promising properties of alkaline earth metal fluorides there is a demand for an easy synthesis access.

While CaF₂ is recovered as mineral fluorite in the nature, the natural occurrence of MgF₂ (Sellaite), SrF₂ (Strontiofluorite) and BaF₂ (Frankdicksonite) is – from an economic point of view – irrelevant. Crystalline MgF₂, SrF₂ and BaF₂ samples are usually prepared by

fluorination with HF, F₂ or other fluorinating agents using the respective carbonates or chlorides under dry conditions or in vacuum [1].

The formation of nanopowders was e.g. described by Glazunova et al. [5] who performed decomposition of trifluoroacetate complexes followed by annealing in an oxygen flow at higher temperature to purify the fluorides from carbon impurities. A solvothermal synthesis of nanocrystalline SrF₂ was described using Sr(CF₃COO)₂ and benzylamine as solvent [14]. General methods for the formation of MF₂ (M: Mg, Ca, Sr, Ba) nanopowders were recently reviewed by Fedorov et al. [15]. They cover methods like thermolysis of trifluoroacetates, sol-gel fluorination, hydro- and solvothermal processes or microwave assisted ionic liquid methods.

The synthesis of nanostructured alkaline earth fluorides by the fluorolytic sol-gel synthesis developed in our group in 2003 [16] is meanwhile well established (s [17] and references therein). As previously demonstrated for CaF₂, another possible synthesis strategy is the mechanochemical route [18]. Using CaCO₃ as educt and NH₄F as fluorinating agent, a phase pure nanocrystalline calcium fluoride could be obtained by milling in a planetary mill [18]. So far, this is the only publication of a mechanochemical preparation of a phase pure alkaline earth fluoride. Attempts to apply this strategy to the synthesis of AlF₃ failed [19].

Mechanochemical studies were reported for nanocrystalline BaF₂, CaF₂ or BaF₂:CaF₂ composite systems with respect to their anionic conductivities [20]. Barium and strontium fluorides as well were used along with lithium fluoride for the preparation of metastable complex ion conductors with inverse perovskite structure [21–23].

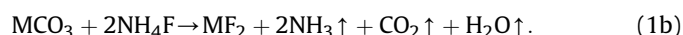
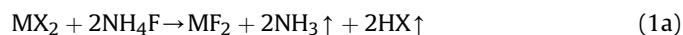
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With the present study the possibility of a fast, easy, direct and solvent free path to nanocrystalline alkaline earth fluorides MF₂ (M: Mg, Ca, Sr, Ba), the mechanochemical synthesis, has been verified.

For this purpose different but comparable metal sources of all alkaline earth metals were used. These are acetates, carbonates, hydroxides and alkoxides (s. Table 1). In all cases ammonium fluoride, NH₄F, was used as fluorinating agent.

The idea is, as demonstrated by the gross equations (1a, b), to initiate a direct fluorination to MF₂ with only volatile byproducts and the alkaline earth fluoride as the only solid product in the grinding bowl:



Moreover, the influence of milling impact, crystal water, humidity, and stoichiometry (M:F ratio) on the product formation was studied.

In addition, beside comparable mechanochemical reactions for all alkaline earth metal compounds (M: Mg, Ca, Sr, Ba) classical solid state chemical reactions of nearly all educt mixtures were performed by thermal annealing in a furnace for comparison.

Analytical methods used in the present study were preferably X-Ray diffraction for phase analysis and ¹⁹F MAS NMR for local structures present in the products.

2. Experimental methods

The alkaline earth metal compounds used for milling experiments were taken as commercially delivered. Their origin, purity and powder diffraction file numbers are summarized in Table 1.

2.1. Mechanical milling

Samples were milled in a commercial planetary mill “Pulverisette 7 premium line” (Fritsch, Germany) both under access of air

and under inert conditions. Each silicon nitride grinding bowl was used with five silicon nitride balls with a ball to powder mass ratio of 14.5. The total powder mass in each grinding bowl was always 1 g, representing a mixture of an alkaline earth metal compound with NH₄F in a stoichiometric ratio M:F as 1:2. If not otherwise indicated samples were milled with a rotational speed of 600 rpm for 4 h. Several magnesium compounds were pre-milled applying the same conditions.

Mechanochemical experiments were performed also with reduced mechanical impact. The weakest possible impact applied was only a manual shaking of 1 g of the stoichiometric educt mixture for 30 s in small plastic beakers without additional grinding balls.

Samples for reactions under inert conditions were dried for 2 days under vacuum and immediately transferred into a glove box.

2.2. Thermal annealing

Classical solid state chemical reactions of stoichiometric educt mixtures were performed in open and closed Pt-crucibles in a high temperature furnace (Carbolite chamber furnace, model RHF 16/3). These educt mixtures were prepared by short shaking in plastic beakers. Closed Pt-crucibles were so called Q-crucibles enabling a quasi-isobaric atmosphere in coexistence with the solid. After a heating rate of 10 K/min each sample was annealed for 2 h isothermally at 900° C and cooled down in the furnace according to Newtons rule.

2.3. XRD and elemental analysis

X-ray diffractograms were measured either on a XRD-7-FPM or a XRD-3003-TT diffractometer (Seiffert & Co., Freiberg) with Cu-K_α radiation (λ = 1.542 Å; 2θ range: 5° ≤ 2θ ≤ 90°; step scan: 0.05°, step time: 5 s). Reflections were compared with diffractograms of the JCPDS-PDF data base [24]. All samples were measured not later than one week after preparation.

Carbon, nitrogen and hydrogen contents were obtained using an EURO EA equipment (HEKAtech GmbH).

The fluoride contents were determined with a fluoride sensitive electrode after conversion of the solids with Na₂CO₃/K₂CO₃ into a soluble form.

2.4. ¹⁹F MAS NMR

¹⁹F MAS NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (Larmor frequency: ν_{19F} = 376.4 MHz) using a 2.5 mm double-bearing magic angle spinning (MAS) probe (Bruker Biospin) and applying a spinning speed of 25 kHz. All spectra were registered with a π/2 pulse duration of 4 μs, a spectrum width of 400 kHz, a recycle delay of 5 or 10 s and accumulation numbers of 16 or 32. The isotropic chemical shifts δ_{iso} of ¹⁹F resonances are given below with respect to the CFCl₃ standard. Existent background signals of ¹⁹F were suppressed with the application of a phase-cycled depth pulse sequence according to Cory and Ritchey [25].

3. Results

Following mechanochemical reactions of alkaline earth metal compounds (s. Table 1) with ammonium fluoride as fluorinating agent to alkaline earth fluorides MF₂ (M: Mg, Ca, Sr, Ba) it became obvious that results can be mainly divided into two groups: fluorides crystallizing in fluorite structure (CaF₂, SrF₂, BaF₂) on the one side, and MgF₂ (rutile structure) on the other side. Therefore, the results presented in the following are subdivided accordingly.

Table 1
Alkaline earth metal compounds used for mechanochemical reactions with ammonium fluoride.

Compound	Origin	Purity	PDF number [24]
Mg(CH ₃ COO) ₂	Research group	Unknown	14–802
Mg(CH ₃ COO) ₂ ·1H ₂ O	ABCR	Unknown	14–828
Mg(CH ₃ COO) ₂ ·4H ₂ O	Aldrich	≥98%	14–827
Mg ₅ (OH) ₂ (CO ₃) ₄ ·4H ₂ O	Riedel	Unknown	25–513
Mg(OH) ₂	de Haen	“Very pure”	44–1482
Mg(CH ₃ CH ₂ O) ₂	Merck	98%	
MgO	Aldrich	≥98%	45–946
Ca(CH ₃ COO) ₂ ·1H ₂ O	Fluka		
CaCO ₃			
Ca(OH) ₂	Aldrich	≥99,0%	44–681
Ca(CH ₃ O) ₂	Merck	≥99%	5–586
	Aldrich	98+ %	44–1481
	Aldrich	97%	20–1565
Sr(CH ₃ COO) ₂ ·0,5H ₂ O			
SrCO ₃	Aldrich	Unknown	43–731
Sr(OH) ₂ ·8H ₂ O		98+ %	5–418
Sr(CH ₃ CH ₂ O) ₂	Aldrich	95%	27–1438
		99.9%	
Ba(CH ₃ COO) ₂	Aldrich	99%	26–131
BaCO ₃	Merck	“For analysis”	45–1471
Ba(OH) ₂ ·8H ₂ O	Aldrich	≥98%	26–155
Ba(CH ₃ CH ₂ O) ₂	Aldrich	99.9%	
NH ₄ F	Aldrich	98+ %	35–758

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