Solid State Sciences 14 (2012) 528–534

Contents lists available at SciVerse ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

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

M. Dreger, G. Scholz*, E. Kemnitz*

Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, D-12489 Berlin, Germany

ARTICLE INFO

Article history:
Received 10 November 2011
Received in revised form
6 January 2012
Accepted 18 January 2012
Available online 31 January 2012

Keywords:
Mechanochemistry
High energy ball milling
Alkaline earth fluorides
NH_4F

ABSTRACT

High energy ball milling as fast, direct and solvent free method allows an easy access to nanocrystalline alkaline earth metal fluorides MF_2 (M: Mg, Ca, Sr, Ba). Comparable metal sources (acetates, carbonates, hydroxides, alkoxides) were used for the reaction with NH_4F as fluorinating agent. Even very simple manual shaking experiments between NH_4F 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.

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 CaF_2 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 CaF_2 is recovered as mineral fluorite in the nature, the natural occurrence of MgF_2 (Sellaite), SrF_2 (Strontiofluorite) and BaF_2 (Frankdicksonite) is – from an economic point of view – irrelevant. Crystalline MgF_2, SrF_2 and BaF_2 samples are usually prepared by fluorination with HF, F_2 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 SrF_2 was described using $Sr(CF_3COO)_2$ and benzylamine as solvent [14]. General methods for the formation of MF_2 (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 CaF_2, another possible synthesis strategy is the mechanochemical route [18]. Using $CaCO_3$ as educt and NH_4F 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 AlF_3 failed [19].

Mechanochemical studies were reported for nanocrystalline BaF_2, CaF_2 or BaF_2:CaF_2 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].

* Corresponding authors. Tel.: +49 30 2093 7455.
E-mail address: Gudrun.Scholz@rz.hu-berlin.de (G. Scholz).

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doi:10.1016/j.solidstatesciences.2012.01.009

With the present study the possibility of a fast, easy, direct and solvent free path to nanocrystalline alkaline earth fluorides MF_2 (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, NH_4F, was used as fluorinating agent.

The idea is, as demonstrated by the gross equations (1a, b), to initiate a direct fluorination to MF_2 with only volatile byproducts and the alkaline earth fluoride as the only solid product in the grinding bowl:

$$MX_2 + 2NH_4F \rightarrow MF_2 + 2NH_3\uparrow + 2HX\uparrow \quad (1a)$$

$$MCO_3 + 2NH_4F \rightarrow MF_2 + 2NH_3\uparrow + CO_2\uparrow + H_2O\uparrow. \quad (1b)$$

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 ^{19}F 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 NH_4F 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.

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

Compound	Origin	Purity	PDF number [24]
$Mg(CH_3COO)_2$	Research group	Unknown	14–802
$Mg(CH_3COO)_2\cdot 1H_2O$	ABCR	Unknown	14–828
$Mg(CH_3COO)_2\cdot 4H_2O$	Aldrich	≥98%	14–827
$Mg_5(OH)_2(CO_3)_4\cdot 4H_2O$	Riedel de Haen	Unknown	25–513
$Mg(OH)_2$	Merck	“Very pure”	44–1482
$Mg(CH_3CH_2O)_2$	Aldrich	98%	
MgO	Fluka	≥98%	45–946
$Ca(CH_3COO)_2\cdot 1H_2O$	Aldrich	≥99,0%	44–681
$CaCO_3$	Merck	≥99%	5–586
$Ca(OH)_2$	Aldrich	98+ %	44–1481
$Ca(CH_3O)_2$	Aldrich	97%	20–1565
$Sr(CH_3COO)_2\cdot 0{,}5H_2O$	Aldrich	Unknown	43–731
$SrCO_3$	Aldrich	98+ %	5–418
$Sr(OH)_2\cdot 8H_2O$	Aldrich	95%	27–1438
$Sr(CH(CH_3)_2O)_2$	Aldrich	99.9%	
$Ba(CH_3COO)_2$	Aldrich	99%	26–131
$BaCO_3$	Merck	“For analysis”	45–1471
$Ba(OH)_2\cdot 8H_2O$	Aldrich	≥98%	26–155
$Ba(CH(CH_3)_2O)_2$	Aldrich	99.9%	
NH_4F	Aldrich	98+ %	35–758

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 ($\lambda = 1.542$ Å; 2Θ range: $5° \leq 2\Theta \leq 90°$; 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 Na_2CO_3/K_2CO_3 into a soluble form.

2.4. ^{19}F MAS NMR

^{19}F MAS NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (Larmor frequency: $\nu_{19F} = 376.4$ 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 registrated with a $\pi/2$ 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 ^{19}F resonances are given below with respect to the $CFCl_3$ standard. Existent background signals of ^{19}F 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 MF_2 (M: Mg, Ca, Sr, Ba) it became obvious that results can be mainly divided into two groups: fluorides crystallizing in fluorite structure (CaF_2, SrF_2, BaF_2) on the one side, and MgF_2 (rutile structure) on the other side. Therefore, the results presented in the following are subdivided accordingly.