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Mechanochemical synthesis, structure and properties of lead containing alkaline earth metal fluoride solid solutions $M_xPb_{1-x}F_2$ (M = Ca, Sr, Ba)

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The paper deals with the mechanochemical synthesis of lead containing alkaline earth metal fluoride solid solutions $M_xPb_{1-x}F_2$ (M = Ca, Sr, Ba) by high-energy ball milling. Several metal precursors and fluorinating agents were tested for synthesizing $M_{0.5}Pb_{0.5}F_2$. Metal acetates and ammonium fluoride as precursors show the most promising results and were therefore used for the formation of $M_xPb_{1-x}F_2$ with different metal cationic ratios. The characterization of the local fluorine coordination and the crystal structure was performed by ^{19}F MAS NMR spectroscopy and X-ray diffraction. Additional calculations of ^{19}F chemical shifts using the superposition model allow a deeper insight into the local structure of the compounds. The fluoride ion conductivity was followed by temperature dependent DC conductivity measurements. Significantly higher conductivities were found in comparison with those of the corresponding binary fluorides. The highest values were observed for samples with high lead content $M_{0.25}Pb_{0.75}F_2$, bearing in mind the much higher conductivity of PbF_2 compared to MF_2.

1. Introduction

In search of more efficient energy capacitors or batteries, solid solutions, especially those containing fluorides crystallizing in the fluorite structure, gain raising interest as possible components in fast fluoride ion conductors [1–4]. Distortions of the local fluoride ion environment by the mutual substitutions of cations while keeping the original crystal structure intact lowers the activation energy for the movement of the fluoride ions [5]. This leads to an increasing ionic conductivity making these compounds potentially applicable as solid electrolytes. The application of such systems however, is not only restricted to electric devices. Replacing one cation with, e.g., a rare earth metal ion allows the preparation of compounds with widely spread use in optics [6–11].

A fast and easy approach to synthesize such systems is the mechanochemical reaction. This branch of synthetic chemistry has got increasing attention during the past years for solid state syntheses [12–14]. While the mechanisms of such reactions can be different and are not completely clear yet, a lot of applications have been developed for this method. It is possible to induce phase transformations of compounds, to modify their surfaces and to enhance their catalytic properties [15]. Non-stoichiometric and/or non- equilibrium products like solid solutions [16–18], co-crystals [19,20] and MOFs [21] can be obtained which are more difficult or excluded to get by common synthesis methods like precipitation or thermally induced reactions. Furthermore, the possibility to avoid using solvents makes mechanochemistry environmentally benign compared to, e.g., the sol-gel-synthesis and may simplify the purification process.

Based on work of Scholz et al. [22,23] we showed in 2016 that it is possible to synthesize $M^a_xM^b_{1-x}F_2$ (M = Ca, Sr, Ba) solid solutions by high energy ball milling [17]. By milling a mixture of metal acetates or hydroxides with ammonium fluoride a mutual substitution of cations over all molar ratios is possible for the Ca/Sr and the Ba/Sr systems. For $Ba_xCa_{1-x}F_2$, the formation of solid solutions was observed only with x > 0.9 or x < 0.1, which may be caused by the size differences of the cations. Conductivity measurements of these systems show significantly increased conductivity values compared

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to the pure binary fluorides. Similar results could be obtained by Heitjans and co-workers [5,16]. Applying an alternative mechanochemical route, namely milling the pure binary fluorides for long durations (up to 99 h), they were able to synthesize even $Ba_xCa_{1\text{-}x}F_2$, although their system is not stable for long times (more than two years) or at elevated temperatures (above 700 K) [5,16]. However here [5,16], the mutual substitution of cations has a positive effect on ionic conductivity.

While mechanochemical synthesis routes have been established for the alkaline earth metal fluorides only little is known for PbF_2. Until 2016, only one mechanochemical synthesis was described in the literature. Subirana-Manzanares et al. [24] published the synthesis of PbF_2 by grinding lead acetate with ammonium fluoride obtaining a paste like compound containing α- and β-PbF_2. Moreover, they were able to direct the formation of either phase by adding organic acids or amines during the reaction. Recently we reported the synthesis of PbF_2 by ball milling different lead precursors with ammonium fluoride [25]. The lead precursor itself determined the formation of the respective PbF_2 phase. The use of lead acetate led to β-PbF_2 (cubic fluorite structure), using lead(II) oxide resulted in mostly α-PbF_2 (orthorhombic structure), and using $PbCO_3$ resulted in a mixture of both phases. As it is beneficial for the formation of solid solutions that both separated binary fluorides crystallize in the same structure, we decided to use for the synthesis of $M_xPb_{1\text{-}x}F_2$ (M = Ca, Sr, Ba) the alkaline earth metal acetates and hydroxides as well as lead acetate and carbonate. All described samples were investigated by X-ray powder diffraction (XRD) and magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy and for selected samples impedance spectroscopy measurements were carried out.

2. Experimental section

2.1. Preparation

All not self-synthesized starting materials were used as commercially purchased (Table 1). The alkaline earth metal fluorides CaF_2, SrF_2 and BaF_2 were synthesized by ball milling (Fritsch Pulverisette 7, premium line) the corresponding metal hydroxides with ammonium fluoride for four hours at 600 rpm. β-PbF_2 with cubic fluorite structure was prepared by heating a mixture of lead acetate trihydrate and ammonium fluoride in a furnace (Eurotherm, Carbolite RHF 16/3) for two hours at 400 °C (heating rate: 10 K/min).

The syntheses of $M_xPb_{1\text{-}x}F_2$ samples were carried out by ball milling the reactants (m = 1 g, ball: powder ≈ 15 g: 1 g; five balls with 12 mm in diameter) for four to eight hours at 600 rpm in silicon nitride beakers (v = 45 ml) according to Scheme 1.

Table 1
Chemicals used in the present study.

Compound	Origin	Purity	PDF number [26]
$Pb(OAc)_2 \bullet 3\ H_2O$	Sigma-Aldrich	≥99%	14–829
$PbCO_3$	Sigma-Aldrich	≥99%	70–2052
PbF_2	self-prepared	–	6-251 (β-phase)
$Ca(OAc)_2 \bullet H_2O$	Sigma-Aldrich	>99%	14–780
$Ca(OH)_2$	Sigma-Aldrich	>96%	44–1481
CaF_2	self-prepared	–	35–816
$Sr(OAc)_2$	Sigma-Aldrich	unspecified	37–655
$Sr(OH)_2$	Sigma-Aldrich	95%	27–847
SrF_2	self-prepared	–	6–262
$Ba(OAc)_2$	Sigma-Aldrich	99%	26–131
$Ba(OH)_2$	Sigma-Aldrich	95%	44–585
BaF_2	self-prepared	–	4–452
NH_4F	Sigma-Aldrich	≥98%	35–758

All samples were dried in a furnace for two hours at 160 °C after reaction if not otherwise stated.

2.2. XRD

X-ray powder diffractograms were measured with an XRD-3003 TT diffractometer (*Seifert*) in the Bragg-Brentano geometry with a range of 2Θ from 5° to 65°. In both cases a CuKα X-ray source (λ = 1.542 Å) was used. The reflections were compared with the JCSPDS-PDF database [26]. Due to the nanocrystalline character of the samples obtained after milling the XRD patterns show typically less intense and broadened reflections. Following that the signal to noise ratio is worse compared to that of crystalline binary fluorides applying the same measurement conditions.

2.3. ^{19}F MAS NMR

A Bruker AVANCE 400 spectrometer equipped with a 2.5 mm magic angle spinning (MAS) probe (Bruker Biospin) was used to record ^{19}F MAS NMR spectra (Larmor frequency: $\nu_{19F} = 376.4$ MHz). All spectra were registered using a $\pi/2$ pulse length of 4 µs, a spectrum width of 400 kHz, a recycle delay of 5 s, an accumulation number of 64, and a rotation frequency of 20 kHz. Recycle delays longer than 5 s were tested to ensure the completeness of the signals and to inspect their spin-lattice relaxation behavior. All isotropic chemical shift values of ^{19}F resonances are given with respect to the $CFCl_3$ standard. Existent background signals were suppressed with the application of a phase-cycled depth pulse sequence according to Cory and Ritchey [27]. The rotor-synchronized spin-echo experiments were registered with a recycle delay of 5 s, an accumulation number of 128 and a dipolar evolution time of 0.5 ms. ^{19}F MAS NMR spectra were simulated using the DMFIT program [28].

2.4. DC conductivity

The conductivity measurements were performed with pellets of 8 mm in diameter and approximately 1 mm in thickness (measured with a Vernier caliper for each pellet). These were obtained from powders by cold pressing, applying a pressure of approximately 800 MPa. Electrodes were applied by coating the pellets with an alcohol based graphite conductive adhesive (Alfa Aesar). DC conductivities were taken from impedance spectra recorded in the frequency range from 0.01 Hz to 10 MHz with a Novocontrol Concept 41 impedance analyzer. The DC conductivity was read out from the frequency independent plateau in the conductivity spectra. The decrease of the conductivity at lower frequencies is caused by the ion blocking electrodes at which the ions accumulate. This decrease also shows that the electronic conductivity is orders of magnitude smaller than the ionic conductivity. Hence, the DC conductivity read out from the conductivity spectra is the ionic conductivity, except for a negligible part caused by electron conduction.

3. Results and discussion

3.1. Synthesis of $Ca_xPb_{1\text{-}x}F_2$

At first, different metal precursors were tested using a molar Ca: Pb ratio of 1: 1. In Fig. 1I, the powder diffractograms for two different reactant compositions and two milling times (4 h and 8 h) are shown. The reactions starting from the metal acetates led to the formation of products whose reflections are located in the middle between those of the pure fluoride references (Fig. 1Ia,b). This indicates, referring to Vegard's Law [29], that solid solutions with a