

Influence of milling, sonication and fluoride doping of pseudoboehmites on their phase transformation behaviour to corundum

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Abstract

The influence of fluoride doping, sonication and milling on the phase transformation of pseudoboehmites to corundum was explored. Followed by XRD and MAS NMR, it can be shown that the crystal structure of the dopant as well as the particle size of the samples is of extreme importance on their thermal behaviour. The combination of ultrasound treatment or rather high energy ball milling and fluoride doping leads to an early beginning of corundum formation at temperatures as low as 700 °C.

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1. Introduction

Today, ceramic materials are widely used but nevertheless the improvement of their properties is of great interest. Especially the fabrication of aluminium oxide engineering ceramics needs easily accessible raw materials (e.g. gibbsite (γ -Al(OH)₃) or pseudoboehmite (AlOOH-xerogel)) of high purity.¹ Due to product properties (high sinter density, high hardness, etc.) and economical reasons, there is a great interest in lowering the temperature of phase transition of the raw material to corundum.^{2–4} In order to reach this goal, two major strategies are possible:

- (1) doping of the raw material (e.g. with metal fluorides) or
- (2) reduction of the particle size of the raw material.

It is well known, that doping of aluminium oxides can reduce the temperature needed to obtain corundum (α -Al₂O₃) considerably. In the literature, several dope additives were tested, but doping of the raw material with corundum and metal fluorides respectively, led so far to the greatest effects (decrease of about 200–300 °C) in lowering the temperature of phase transition to corundum.^{5–9} The second option, particle size reduction of the

raw material, can be achieved by several methods.^{10–13} It is an established fact, that small particle sizes result in lowered transition temperatures.^{10,14,15} The most popular technique is the sol-gel synthesis of pseudoboehmite, which leads to particle sizes in the micrometer range.^{12,13} Another, even more powerful, method to produce small particle sizes is high energy ball milling.^{16,17} By using this method, the temperature of phase transition to corundum can be lowered down to ~910 °C.¹⁴ A less considered alternative to form small particles is the sonication of precursor substances.^{11,18–21}

In the present paper three major types of doped and undoped AlOOH-xerogels were prepared (Scheme 1): common pseudoboehmite (by using a classical sol-gel synthesis route), milled pseudoboehmite (milling of the dry xerogel obtained by sol-gel synthesis) and sonicated pseudoboehmite (sonication in the sol state). The different treatment of the xerogels leads to varying particle sizes and structural disturbances. Additionally, we doped the pseudoboehmites with different aluminium fluorides (α -AlF₃, *a*-AlF₃ and *HS*-AlF₃-precursor).

Therefore, the aims of the present study are:

- (i) to compare the influence of milling and sonication on the phase transition behaviour from pseudoboehmite to corundum,
- (ii) to compare the influence of the different fluoride dope additives on the phase transition to corundum, and

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- (iii) to combine the different synthesis routes with fluoride doping to compare these effects on the phase transition to corundum, and to obtain corundum at temperatures as low as possible.

2. Experimental

Aluminium *sec*-butoxide (98%) was purchased from ABCR, α -AlF₃ (99%) was purchased from Aldrich and nitric acid (65 wt%) was purchased from J. T. Baker.

An overview of the synthesis ways to the different doped and undoped pseudoboehmites is given in Scheme 1.

Preparation of amorphous AlF₃ (a-AlF₃): α -AlF₃·3H₂O was heated to 200 °C (5 °C/min, 2 h dwell time) in a Q-crucible (ensures quasi-equilibrium conditions of the solid with its own gaseous phase) to obtain amorphous AlF₃.

Preparation of HS-AlF₃-precursor (AlF₃·1.12H₂O)²²: The *high-surface* aluminium fluoride precursor was prepared using Schlenk techniques under argon atmosphere because the precursor compound is moisture-sensitive and the product tends to adsorb water. Tetrahydrofurane (THF) was dried over Na and distilled prior to use. Aluminium *iso*-propoxide and hydrofluoric acid (50 wt%) were purchased from Aldrich. Aluminium *iso*-propoxide was dissolved in 100 ml dry THF to avoid an uncontrolled hydrolysis. Then, the hydrofluoric acid was slowly added in molar ratio Al:F = 1:3 under stirring at room temperature. The resulting sol was stirred for 20 min followed by the removal of the solvent and formed *iso*-propanole under

reduced pressure. The final product was dried at 180 °C under vacuum.

Preparation of doped and undoped pseudoboehmite (AlOOH-xerogel)²³: Relating to aluminium *sec*-butoxide (ASB), 13 mol% dopant (α -AlF₃, a-AlF₃, HS-AlF₃-precursor) was dispersed in water which was heated to a temperature of 90 °C and stirred at high speed. The boehmite-sol was prepared by adding aluminium *sec*-butoxide to this mixture. The solution was kept at 90 °C and, 45 min after addition of the alkoxide, 0.6 mol HNO₃ per mol alkoxide was added to peptize the sol particles. Following, the sol was stirred for another hour at 90 °C. The sol was concentrated by evaporation and dried to constant weight at 120 °C.

Preparation of milled pseudoboehmites (doped and undoped): High energy ball milling of pseudoboehmites (synthesis as described before) was performed in a commercial planetary mill “Pulverisette 7” (Fritsch, Germany) under the access of air applying milling times of 4 h. Each syalon vial was used with five syalon balls (m_{balls} : 14.8 g; m_{sample} : 1 g) and a rotational speed of 600 rpm (rpm: rotations per minute) was applied.

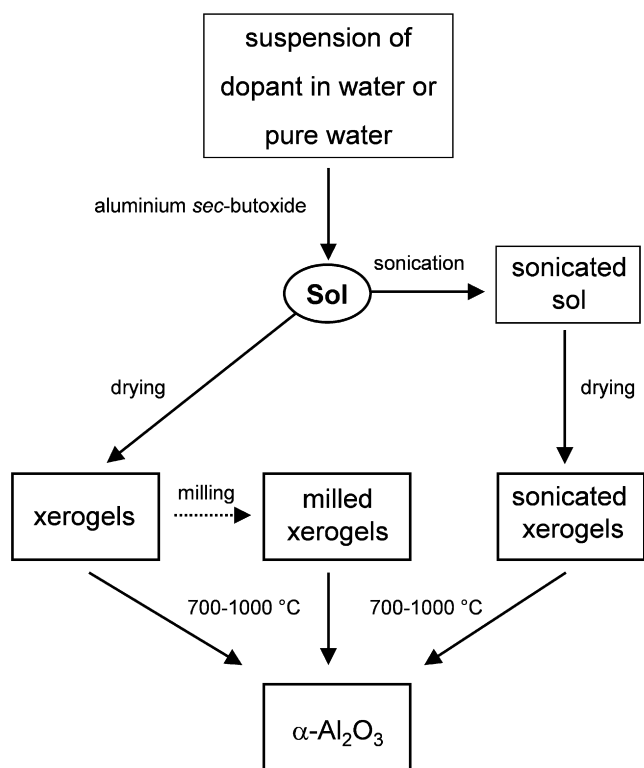
Preparation of ultrasound treated pseudoboehmite (doped and undoped): Relating to aluminium *sec*-butoxide, 13 mol% dopant (α -AlF₃, a-AlF₃, HS-AlF₃-precursor) was dispersed in water which was heated to 90 °C and stirred at high speed. The boehmite-sol was prepared by adding aluminium *sec*-butoxide to this mixture. The solution was kept at 90 °C and, 45 min after addition of the alkoxide, 0.6 mol HNO₃ per mol alkoxide was added to peptize the sol particles. Following, the sol was stirred for another hour at 90 °C. The sonication (3 h, frequency: 35 kHz, High Frequency power: 300 W_{eff}) was performed in a “Sonorex Super RK 1028 H” (Bandelin, Germany). Afterwards the sol was concentrated by evaporation and dried to constant weight at 120 °C.

The thermal treatment of the samples was performed in a tube furnace in flowing air (20 ml/min). To produce a moist atmosphere (moist air), the flowing air was piped through a water filled bubble counter. The samples were calcined (heating rate 20 °C/min) between 700 and 1000 °C (dwell time 4 h). Although calcination of ceramics usually is performed under dry air conditions, calcination under moist air has been included in these investigations since it was shown that aluminium fluoride undergoes a remarkable pyrohydrolysis reaction in the presence of moisture ($\text{AlF}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + 3\text{HF}$). Consequently it was the aim to elucidate what kind of impact on the calcination behaviour of corundum may originate from this fact.²²

For X-ray powder diffraction measurements a Seifert XRD 3003 TT equipment (Freiberg, Germany) with Cu K α radiation was applied. Phases were identified by comparison with the ICSD powder diffraction database.²⁴

For scanning electron microscopy (SEM) measurements a scanning electron microscope JSM-60460 SEM (Jeol Ltd., Tokyo, Japan) machine was used.

MAS NMR spectra were recorded at spinning speeds of 25 and 30 kHz and resonance frequencies of 376.4 MHz for ¹⁹F and 104.6 MHz for ²⁷Al on a Bruker AVANCE 400 spectrometer equipped with a 2.5 mm MAS probe.



Scheme 1. Preparation of different types of (fluoride-doped) xerogels by: classical sol-gel synthesis, milling of the dry xerogels and sonication in the sol state and their subsequent treatment to Al₂O₃.

Table 1
Composition and pre-treatment of the samples.

Sample name	Composition	Synthesis
A	AlOOH	Sol-gel
B	AlOOH/HS-AlF ₃ -precursor	Sol-gel
C	AlOOH/a-AlF ₃	Sol-gel
D	AlOOH/α-AlF ₃	Sol-gel
SA	AlOOH	Sonication
SB	AlOOH/HS-AlF ₃ -precursor	Sonication
SC	AlOOH/a-AlF ₃	Sonication
SD	AlOOH/α-AlF ₃	Sonication
MA	AlOOH	Milling
MB	AlOOH/HS-AlF ₃ -precursor	Milling
MC	AlOOH/a-AlF ₃	Milling
MD	AlOOH/α-AlF ₃	Milling

a-AlF₃: Amorphous AlF₃.

¹⁹F MAS NMR ($I = 1/2$) spectra were recorded with a $\pi/2$ pulse duration of $p1 = 2 \mu\text{s}$, a spectrum width of 400 kHz, a recycling delay of 10 or 20 s, and an accumulation number of 16 or 32. Isotropic chemical shifts of ¹⁹F are given with respect to the CFCl₃ standard. Background signals of ¹⁹F could be completely suppressed with the application of a phase-cycled depth pulse sequence according to Cory and Ritchey.²⁵

²⁷Al MAS NMR ($I = 5/2$) spectra were recorded with excitation pulse duration of 1 μs . A 1 M aqueous solution of AlCl₃ was used as reference for the chemical shift of ²⁷Al. The recycle delay was chosen as 1 s and the accumulation number was 20 000.

Table 2
Phases identified by XRD after annealing at 1000 °C.

Sample	Corundum	Transition aluminas (ϵ , γ , δ , θ and σ forms)
A	d	+
SA	+	~
MA	+	d

+: Major component; ~: minor component; d: detectable.

3. Results and discussion

The composition, synthesis method and notation of the different samples used, are shown in Table 1. The wide influence of different sample pre-treatments on the thermal behaviour of undoped pseudoboehmites is shown in Table 2 and Figure EA1 (see Electronic Annex 1 in the online version of this article.). The different particle sizes of untreated (A; Fig. 1, a), sonicated (SA; Fig. 1, b) and milled (MA; Fig. 1, c) pseudoboehmites obtained by SEM measurements are depicted in Fig. 1. The decreasing particle sizes (decrease from untreated over sonicated to milled) leads after thermal treatment at 1000 °C to an earlier corundum formation.¹⁴ The comparatively large particles of the untreated pseudoboehmite (A) mainly show weak reflections of transition aluminas in the diffractogram (Table 2 and Figure EA1, a), but a little amount of corundum is already detectable by XRD. The sonication of the pseudoboehmite (SA) in the sol state results in a wide distribution of the particle size (Fig. 1, b). There are large as well as very small particles existent. These small particles can undergo an “early” phase transition to corundum¹⁴ and

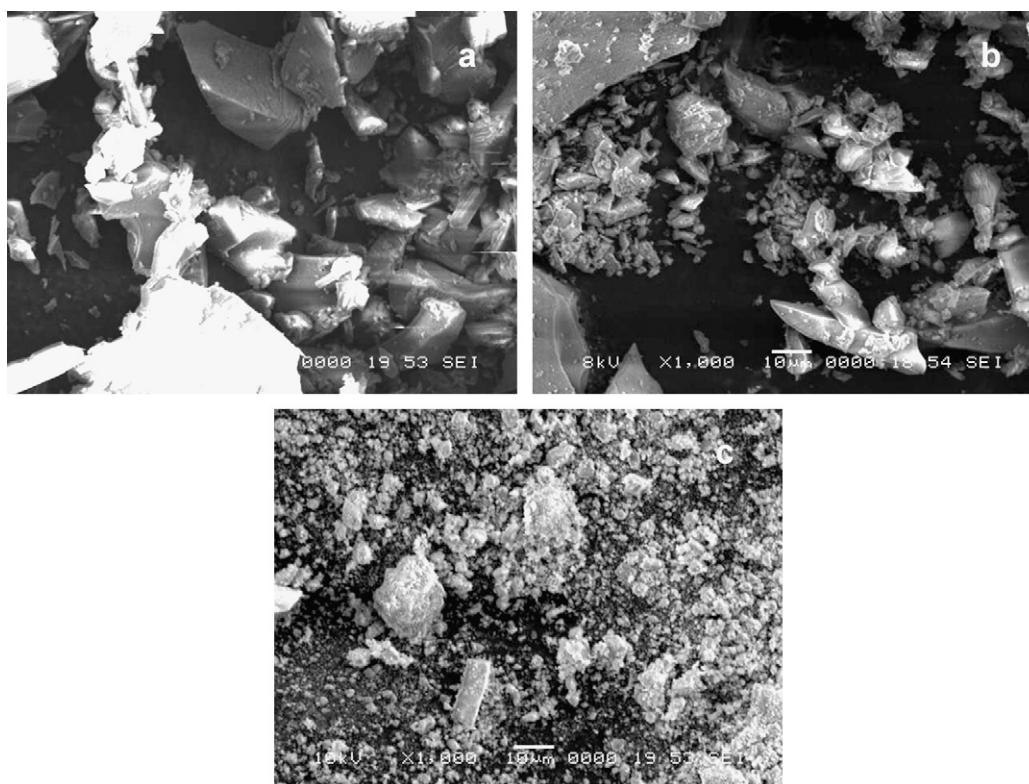


Fig. 1. SEM images of pseudoboehmite xerogels after synthesis. 1000 times magnified. (a: without additional treatment (A); b: 3 h ultrasound treated in the sol state (SA); c: 4 h milled (MA)).

act as seeds. This “in situ corundum seeding” of the boehmite xerogel lowers the phase transition temperature to corundum, additionally.⁷ Both effects result in a higher amount of corundum after the annealing of SA (Table 2 and Figure EA1, c). The milled pseudoboehmite (MA) exhibits the smallest particle sizes. Therefore, the phase transition to corundum takes place already completely at 1000 °C (Table 2 and Figure EA1, b). Additionally, a seeding effect caused by milling can be discussed. During milling, local temperatures up to ~1500 °C and local pressures of more than 1×10^8 Pa can occur.²⁶ Under these extreme conditions, the generation of corundum seeds without additional annealing can take place.²⁷

The effect of the fluoride additives on the phase transition is obviously primarily dependent on the similarity of the crystal structure to α -Al₂O₃.⁶ Additives with a crystal structure different from α -Al₂O₃ have less or no effects on the phase transformation to α -Al₂O₃. Corundum and α -AlF₃ have a very similar crystal structure (same space group). HS-AlF₃-precursor and a-AlF₃ are amorphous compounds and therefore the effects on the phase transition should be less characteristic than by α -AlF₃.

In Fig. 2-1 the X-ray diffractograms of doped (Fig. 2-1, b–d) and undoped (Fig. 2-1, a) pseudoboehmites obtained by sol–gel

synthesis after thermal treatment at 900 °C are shown. After annealing at 900 °C undoped and untreated pseudoboehmite (A; Fig. 2-1, a) only show reflections of transition aluminas. Annealing of HS-AlF₃-precursor-doped pseudoboehmite (B; Fig. 2-1, b) produces corundum beside transition aluminas. Comparable results were obtained by the annealing of a-AlF₃-doped pseudoboehmite (C; Fig. 2-1, c). Again, there is a corundum phase beside a mixture of transition aluminas, but the content of corundum is, compared with sample B (Fig. 2-1, b), slightly lower. Obviously, even the fluoride doping with amorphous aluminium fluorides has an effect on the phase transformation. Because of the similarity with the crystal structure of corundum, doping with α -AlF₃ has the biggest effect (D; Fig. 2-1, d). The diffractogram only shows a single corundum phase with narrow reflections.

At this point, the influence of the different synthetic routes (i) and the influence of fluoride doping (ii) on the phase transformation to corundum seems obvious. The particle size reduction of the pseudoboehmite (and therefore the increase of surface energy and defect concentration) has a great influence on the transformation temperature and the phase purity of the final corundum. But the fluoride doping also causes a clear decrease of the transformation temperature because of the different (crystal) structure of the dope additives.

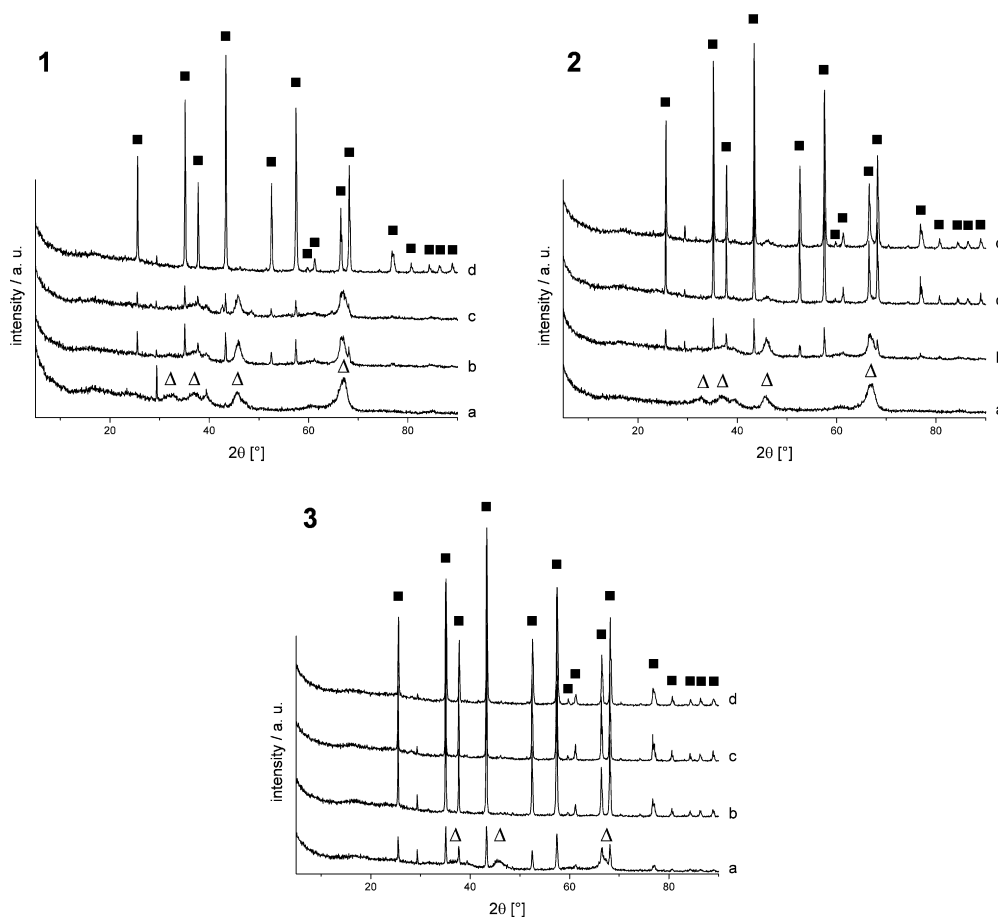


Fig. 2. X-ray powder diffractograms of untreated (1), ultrasound treated (2) and milled (3) pseudoboehmites doped with different aluminium fluorides after thermal treatment (4 h at 900 °C, 20 °C/min) in moist air. (a: pseudoboehmite, without doping; b: pseudoboehmite, doped with HS-AlF₃-precursor; c: pseudoboehmite, doped with a-AlF₃; d: pseudoboehmite, doped with α -AlF₃; ■: reflections of α -Al₂O₃; Δ: reflections of transition aluminas (ϵ , γ , δ , θ and σ forms)).

The influence of sonication in the sol state on the corundum formation is shown in Fig. 2-2. Whereas the annealing of sonicated AlOOH-xerogel at 1000 °C (SA; Table 2 and Figure EA1, c) leads to a phase mixture of transition aluminas beside a major corundum phase, the thermal treatment of the same sample at 900 °C (SA; Fig. 2-2, a) produces only transition aluminas. Compared with the un-sonicated pseudoboehmite (A; Fig. 2-1, a), an effect of sonication is not visible. Analogue results were obtained by the annealing of sonicated, HS-AlF₃-precursor-doped pseudoboehmite (SB; Fig. 2-2, b). In this case too, the diffractograms of the sonicated and the un-sonicated sample (B; Fig. 2-1, b) are very similar. Obviously, particle size reduction by ultrasound treatment combined with HS-AlF₃-precursor-doping of the pseudoboehmite is insufficient to decrease the phase transition temperature to corundum. Otherwise, the sonication of α -AlF₃-doped AlOOH-xerogel leads to an almost complete corundum formation after thermal treatment at 900 °C (SC; Fig. 2-2, c). As expected, sonication combined with α -AlF₃-doping (SD; Fig. 2-2, d) yields a complete corundum formation after annealing at 900 °C whereas the influence of α -AlF₃-doping prevails. Based on all these findings, the influence of the different fluoride dope additives on the phase transformation behaviour can be defined. The ability of lowering the temperature of phase transition to corundum rises in the sequence HS-AlF₃-precursor < α -AlF₃ << α -AlF₃ (Table 3). These findings correspond very well with the thermal behaviour of the used fluorides themselves. Annealing of HS-AlF₃-precursor in moist air (as applied here) leads to pyrohydrolysis of the Al-F-bonds and therefore to a generation of corundum seeds.²² A crystallization to α -AlF₃ does not take place.²² Amorphous aluminium fluoride (α -AlF₃) crystallizes in the sequence α -AlF₃ → β -AlF₃ → α -AlF₃ in a broad temperature interval of ~ 200 °C.^{28,29} This crystallization sequence is beginning at about 300 °C.^{28,29} Because of that, not only pyrohydrolysis (and therefore corundum seeding) take place, but there are also effects of the crystallized β -AlF₃ and even of α -AlF₃ with its similar crystal structure to corundum.

The biggest effect on the phase transformation behaviour, compared with sonication and sol-gel synthesis, is caused by high energy ball milling (Table 3). Fig. 2-3 shows the X-ray diffractograms of milled pseudoboehmites (doped and undoped) after thermal treatment at 900 °C. The milled samples, doped with HS-AlF₃-precursor (MB; Fig. 2-3, b), α -AlF₃ (MC; Fig. 2-3, c) as well as α -AlF₃ (MD; Fig. 2-3, d), all produce corundum as the only phase after annealing at 900 °C. The effect of milling

is superimposed by fluoride doping, but nevertheless essential to reduce the temperature of phase transition down to 900 °C. This fact is depicted in the diffractogram of the milled, undoped pseudoboehmite (MA; Fig. 2-3, a), which shows corundum beside transition alumina reflections.

To investigate the abilities of fluoride doping, sonication and milling on the thermal behaviour of pseudoboehmites, the samples were annealed at 800 °C. In Table 4 and Figure EA2 (see Electronic Annex 2 in the online version of this article.), all diffractograms of samples which contain corundum reflections are shown. Again, milling of the fluoride-doped samples appears to be the promising way of corundum generation. However, the type of fluoride, used as dope additive is also of great influence. The best results were obtained using α -AlF₃ as dope additive. Within this composition, the milled sample (MD; Table 4 and Figure EA2, f) contains the highest amount of corundum beside residual transition aluminas. The sonicated sample (SD; Table 4 and Figure EA2, e) also shows reflections of corundum, but the amount of transition aluminas is higher and there are residues of α -AlF₃ detectable. Even the untreated α -AlF₃-doped pseudoboehmite (D; Table 4 and Figure EA2, d) begins to form corundum, and thus, transition aluminas and residues of α -AlF₃ are detectable. The use of α -AlF₃ as dope additive leads to a less corundum formation after thermal treatment at 800 °C. The content of corundum fades in the sequence: milled α -AlF₃-doped pseudoboehmite (MC; Table 4 and Figure EA2, c), sonicated α -AlF₃-doped pseudoboehmite (SC; Table 4 and Figure EA2, b) and untreated α -AlF₃-doped pseudoboehmite (C; Table 4 and Figure EA2, a). It is noteworthy, that the untreated α -AlF₃-doped pseudoboehmite (D; Table 4 and Figure EA2, d) exhibits a higher corundum content than the milled α -AlF₃-doped pseudoboehmite (MC; Table 4 and Figure EA2, c). This finding illustrates the influence of the dope additive in contrast to the synthesis method.

A surprising result delivers the thermal treatment of milled HS-AlF₃-precursor doped pseudoboehmite at 800 °C (MB; Table 4 and Figure EA2, g). Here, the content of formed corundum is unexpectedly high, whereas the other two HS-AlF₃-precursor-doped pseudoboehmites generate no corundum at this temperature. This finding is explainable by the small particle size caused by high energy ball milling, which leads to an earlier pyrohydrolysis and therefore to a complete corundum conversion of the dope additive.³⁰

The XRD patterns of all samples which show corundum reflections even after thermal treatment at only 700 °C are shown in Figure EA3 (see Electronic Annex 3 in the online version of this article.) and the identified phases are summarised in Table 4. As expected, the α -AlF₃-doped samples display the different influence of the synthesis conditions on the corundum formation. The best results were obtained by milling of α -AlF₃-doped pseudoboehmite (MD; Table 4 and Figure EA3, c). The diffractogram consists of two phases, a major transition alumina phase and a corundum phase. In XRD no residual α -AlF₃ is detectable. Due to the beginning local corundum formation at temperatures as low as 700 °C which might be covered by XRD, solid state NMR measurements were performed in addition. The ²⁷Al

Table 3
Summary of the corundum formation in dependence on the sample pre-treatment.

Dopant	Corundum formation after activation by		
	None	Sonication	Milling
α -AlF ₃	+	+	+
α -AlF ₃	~	+	+
HS-AlF ₃ -precursor	~	~	+
none	-	-	~

+: Complete corundum formation at 900 °C; ~: partial corundum formation at 900 °C; -: no corundum formation at 900 °C.

Table 4
Phases identified by XRD after annealing at 800 °C and 700 °C.

Sample	Phases after annealing at 800 °C			Phases after annealing at 700 °C		
	α -Al ₂ O ₃	AIOOH ^a	α -AlF ₃	α -Al ₂ O ₃	AIOOH ^a	α -AlF ₃
C	d	+	–	–	+	–
SC	d	+	–	–	+	–
MC	~	+	–	–	+	–
D	~	+	d	d	+	d
SD	~	+	d	d	+	d
MD	+	~	–	~	+	–
MB	+	~	–	d	+	–

+: Major component; ~: minor component; d: detectable; –: not detectable.

^a Transition aluminas (ϵ , γ , δ , θ and σ forms).

and ¹⁹F MAS NMR spectra of the milled α -AlF₃-doped pseudoboehmite (**MD**) before and after thermal treatment at 700 °C are given in Fig. 3. The unannealed sample shows four peaks in the ²⁷Al spectrum. The signals at 28 and 60 ppm stand for five-fold and four-fold coordinated Al-species,^{31,32} respectively, and therefore for the high disturbance of the pseudoboehmite generated by high energy ball milling. The signal at 6 ppm stands for six-fold oxygen-coordinated Al in AIOOH³¹ while the ²⁷Al signal at –16 ppm and the ¹⁹F signal at –173 ppm are typical for α -AlF₃.^{33–35} After thermal treatment at 700 °C, the ²⁷Al spectrum of **MD** (Fig. 3) shows the typical spectral pattern of γ -Al₂O₃^{31,32,36,37} with two peaks at 63 and 10 ppm. The ¹⁹F spectrum (Fig. 3) consists of weak signals in the range of –130 to –143 ppm with a worse signal-to-noise ratio. They represent residual AlF_xO_{6–x} octahedra ($x \leq 2$)^{33,34} in the matrix and

evidences the high degree of α -AlF₃-decomposition caused by pyrohydrolysis.

An explicit corundum signal (13 ppm) is not visible, but the broadness and the asymmetry of the main signal at 10 ppm could mask it. Nevertheless the shape of the spinning sidebands of the ²⁷Al spectra is already very similar to that of corundum (Fig. 4).

The diffractogram of sonicated α -AlF₃-doped AIOOH-xerogel (**SD**; Table 4 and Figure EA3, b) also shows corundum reflections after annealing at 700 °C, but the content of α -Al₂O₃ is less than in the milled sample (**MD**). Additionally, there are reflections of residual α -AlF₃ detectable. The comparatively large particle size of the sonicated sample, connected with the relative low annealing temperature is not sufficient to form a higher amount of corundum and to decompose the α -AlF₃ completely (pyrohydrolysis).

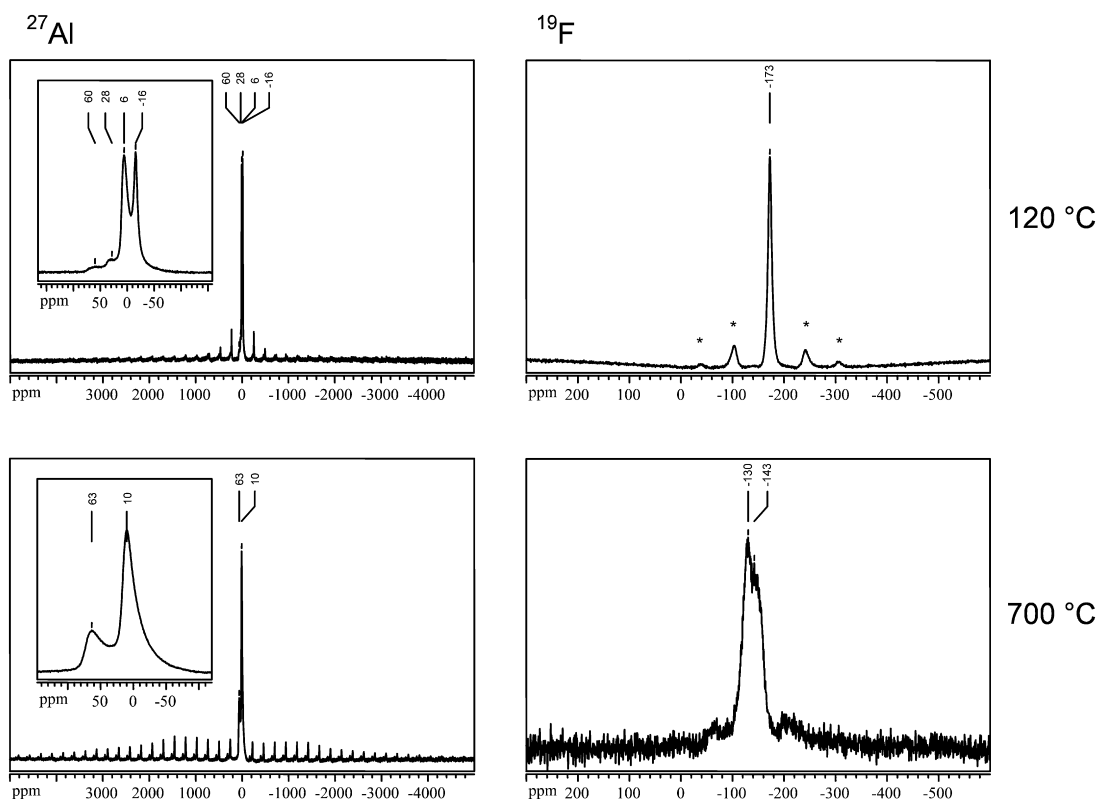


Fig. 3. ²⁷Al and ¹⁹F MAS NMR spectra of α -AlF₃-doped, milled pseudoboehmite (**MD**) before and after thermal treatment at 700 °C. All measurements were performed at a spinning speed of 25 kHz (*, spinning sidebands).

The untreated α -AlF₃-doped pseudoboehmite (**D**; Table 4 and Figure EA3, a) has, compared to **MD** and **SD**, the largest particle size. Therefore, the content of corundum, detected by XRD, is the lowest. Again, there are residues of α -AlF₃ beside transition aluminas as main component. In the ²⁷Al MAS NMR spectrum of the unannealed sample two signals are visible (Figure EA4, see Electronic Annex 4 in the online version of this article). The peak at 7 ppm represents the six-fold oxygen-coordinated Al in AlOOH³¹, whereas the signal at -16 ppm is typical for ²⁷Al in α -AlF₃.^{34,35} In contrast to the ²⁷Al spectrum of **MD** (Fig. 3) there are no hints of four-fold or five-fold coordinated Al-species. The ¹⁹F MAS NMR spectrum (Figure EA4) only shows one single α -AlF₃-peak at -173 ppm.^{33–35} In the ²⁷Al MAS NMR spectrum of the annealed sample (**D**, Figure EA4) two signals at 64 and 7 ppm stand for γ -Al₂O₃ as main component beside other transition aluminas.^{31,32,36,37} Again, the broad signal at 7 ppm may cover a corundum peak at 13 ppm. Also in this case the shape of the spinning sidebands indicates an early corundum formation superimposed by those of the pseudoboehmite (Fig. 4). In the ¹⁹F spectrum (Figure EA4, see Electronic Annex 4 in the online version of this article.) only weak signals in the range of -133 to -174 ppm with a worse signal-to-noise ratio were detected. Obviously, residual AlF_xO_{6-x} units ($x \leq 3$) and rests of α -AlF₃^{33,34} (-174 ppm) are still present in the matrix.

The diffractogram of annealed *HS*-AlF₃-precursor-doped pseudoboehmite (**MB**; Table 4 and Figure EA3, d) also shows weak reflections of corundum beside transition aluminas as main component. But again, the small particle size caused by high energy ball milling leads to an earlier beginning of pyrohydrolysis and therefore all dope additive is converted to corundum.³⁰ The MAS NMR spectra of **MB** (Figure EA5, see Electronic Annex 5 in the online version of this article.) support that finding. Because of the milling, there are five-fold coordinated Al-species (30 ppm)^{31,32} beside AlOOH (5 ppm)³¹ and AlF₆-species (-16 ppm)^{22,33,34} detectable. The ¹⁹F spectrum of **MB** consists of a signal at -145 ppm (AlF_xO_{6-x}, $x \leq 3$)^{22,33,34} and a shoulder at -165 ppm which is a clear argument for the existence of AlF_xO_{6-x} with $x \cong 5$ ^{22,33,34} and a typical value for the *HS*-AlF₃-precursor. After annealing at 700 °C, the ²⁷Al spectrum (Figure EA5) shows the two γ -Al₂O₃ signals at 63 and 6 ppm.^{31,32,36,37} Again, the shape of the spinning sidebands begins to form the typical corundum shape (Fig. 4). The ¹⁹F spectrum of **MB** consists of weak signals in the range of -128 to -145 ppm with worse signal-to-noise ratio, representing residual AlF_xO_{6-x} octahedra ($x \leq 2$)^{33,34} in the matrix. The comparison of the ²⁷Al spectra of the annealed samples **MB**, **D** and **MD** show a high field shift of the main signal from 6 ppm (**MB**) over 7 ppm (**D**) to 10 ppm (**MD**). This behaviour, as well as the equalisation of the shape of the spinning sideband on that of corundum (Fig. 4), corresponds very well with the increasing corundum content of the samples.

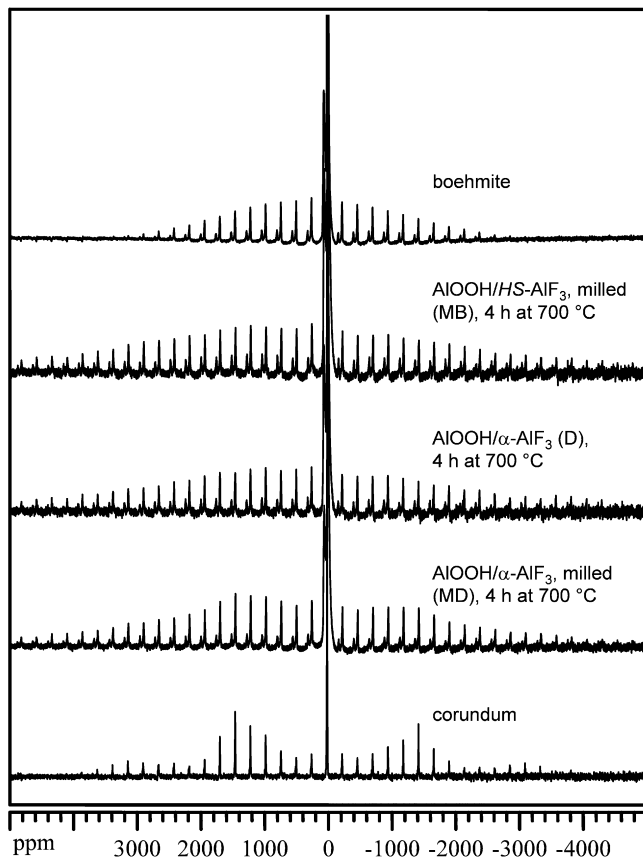


Fig. 4. ²⁷Al MAS NMR spinning sideband shape comparison of **MB**, **D** and **MD** after annealing at 700 °C with the spinning sidebands of boehmite and corundum. All measurements were performed at a spinning speed of 25 kHz.

4. Conclusion

In the presented paper, the influence of milling and sonication on the thermal behaviour of fluoride-doped AlOOH-xerogels was investigated. It turns out, that doping with α -AlF₃ has the most pronounced effect on the phase transition behaviour to corundum. Independent from the synthesis route (sol-gel, sonication or milling), all α -AlF₃-doped samples completely form corundum at 900 °C, because of the similarity of the crystal structure of corundum and α -AlF₃.⁶ The use of amorphous AlF₃ (*a*-AlF₃) as dope additive is less effective. Although a phase transformation to α -AlF₃ takes place at annealing,^{28,29} doping of pseudoboehmite with *a*-AlF₃ without additional activation is not sufficient to produce corundum at 900 °C under the conditions applied here. Because of the disability of *HS*-AlF₃-precursor to crystallise to α -AlF₃,²² the observed effects in temperature decrease of the phase transition are caused by pyrohydrolysis effects. Nevertheless, the particle size has an enormous influence on the phase transformation behaviour. Milling of the undoped sample leads to a complete corundum formation after annealing at 1000 °C. The temperature of phase transition can be lowered from temperatures above 1200 to 1000 °C by small particle sizes (Table 2 and Figure EA1). Also, sonication leads to a particle size reduction and therefore to an almost complete corundum formation at 1000 °C.

The best results were obtained by the combination of both techniques (for a summary of the results, see Table 3). High energy ball milling combined with fluoride doping leads in all cases to a complete corundum formation after thermal treat-

ment at 900 °C. But the sonicated, α -AlF₃ and α -AlF₃-doped pseudoboehmites also form corundum as the only phase after annealing.

The enormous potential of α -AlF₃ doping and milling is displayed by the ability to begin to form corundum even at 700 °C (Fig. 4).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jeurceramsoc.2009.04.002.

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