Synthesis of Nanocrystalline NH$_4$MnF$_3$. A Preparation Route To Produce Size-Controlled Precipitates via Microemulsion Systems

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Using ammonium-substituted AOT as surfactant and *n*-heptane as dispersion medium, water in oil microemulsions with large contents of concentrated NH$_4$F and manganese acetate aqueous solutions, respectively, have been stabilised. After mixing, nanostructured NH$_4$MnF$_3$ precipitates, in spite of its comparatively high solubility in water. During the coagulation with acetone, CH$_3$COONH$_4$(s) is formed which, however, can quantitatively be removed by transformation into acetamide and subsequent solution in the organic medium. The resulting *n*-NH$_4$MnF$_3$ is immediately crystalline at room temperature without annealing procedures. Different mean crystallite sizes between 10 and 60 nm were obtained by appropriate variation of the synthesis parameters, i.e., aqueous phase content, salt concentration, synthesis temperature, and the period of time between the mixing of the two microemulsions and the coagulation with acetone.

1. Introduction

Nanophase ceramics with an average size of less than 100 nm have generated considerable scientific interest because of the improvements in a variety of properties that are expected to result from the reduced grain size. Impressive examples are the significant lowering of sintering temperatures of ceramic powders and the increased mechanical strength of ceramic components due to improved homogeneity and controlled particle size distribution in green bodies. An excellent survey of syntheses, characterizations, and properties of nanoscale materials is given in a special edition of *Chemistry of Materials.*[1]

In our study, we used a microemulsion (ME) method to synthesize tailored ultrafine crystals of NH$_4$MnF$_3$, an antiferromagnetic salt which on the one hand can serve as a model substance to investigate the preparation route of nanoscale inorganic salts by using microemulsions. On the other hand, NH$_4$MnF$_3$ exhibits a model-like Heisenberg antiferromagnetism[2] with a Néel temperature of 84 K for coarse grained material.[3] The material in the nanocrystalline form should allow for the study of nano-antiferromagnetism.[4]

In contrast to macroemulsions, microemulsions are isotropic, optically transparent, thermodynamically stable dispersions of oil in water (o/w-microemulsion) or water in oil (w/o-microemulsion). Such dispersions form spontaneously by mixing the two liquids with a surfactant and, if necessary, a medium length alcohol (cosurfac-

Table 1. Examples of Precipitates Produced via Microemulsion Systems

substance/reference	particle size, nm	isolation as a powder?	employed salts and reagents
AgCl[10,11]	8	no	NaCl, AgNO$_3$
	5–10		
TiO$_2$[9]	20–50	yes	TiCl$_2$, NH$_3$
CdS[12]	5	no	CdNO$_3$, H$_2$S
Fe$_3$O$_4$[13]	3–5	no	FeCl$_2$, FeCl$_3$, NH$_3$
CdS, CuS, PbS, In$_2$S$_3$[14]	5	no	perchlorates, H$_2$S

tant).[5,6] If the water is the dispersed phase, the surfactant and the water form socalled reversed micelles. The essential feature of the ME synthesis techniques is the ability to restrict reactions in a wet chemical system to the socalled nanoreactors of the reversed micelles as has recently been demonstrated for a sol-gel type synthesis of nanocrystalline oxides.[7] A review of the syntheses of nanosized particles in microemulsions is given in ref 8. One of the possible ME-mediated synthesis routes is the precipitation of particles by mixing two w/o-microemulsions containing soluted salts in the aqueous cores.[9] Table 1 comprises a literature review of powder syntheses using precipitation in a ME system. The examples elucidate the difficulties:

1. It is not a trivial problem to isolate the nanoscale particles from the ME system for the following reasons: (i) particles can agglomerate while being separated from the sol; (ii) often the yields are very low due to the small amount of salt solution which can be stabilized in the ME system.

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2. The counterions, for example NO_3^- and Na^+ in the AgCl -precipitation,[10,11] contaminate the product. In some cases these byproducts can be removed by sublimation at higher temperatures, but this implies a growth of the crystallites which is not desired for nanocrystalline materials.

Particularly the ME-mediated synthesis of NH_4MnF_3 involves many problems: (1) Compared to that of the examples given in Table 1, the solubility of NH_4MnF_3 is relatively high (12 g in 1 L H_2O at 20 °C[15]) so the precipitation yield is drastically reduced. Therefore large amounts of highly concentrated salt solutions must be stabilized in the microemulsions to compensate the loss of yield. This stabilization, however, is hindered by the salting out effect: The higher the salt concentration of a solution is, the less the aqueous solution may be stabilized in a microemulsion system.[16] A theory of the salting-out effect is given by Beunen and Ruckenstein.[17] (2) After precipitation a sol with low colloidal stability is formed in which the primary nanoscale particles rapidly grow due to agglomeration; this has to be prevented. (3) Processing of the raw product at elevated temperatures is not possible because NH_4MnF_3 decomposes to NH_4F and MnF_2 at higher temperatures (310 °C); furthermore, in the presence of O_2 the salt may be oxidized to MnO_2. Therefore, in order to obtain a chemical pure product an indulgent method to purify the particles had to be developed.

In spite of these difficulties, nano-NH_4MnF_3 can efficiently be prepared with varying mean grain sizes and reasonably narrow grain size distributions, as will be described in the present contribution.

2. Experimental Procedure

2.1. Chemicals. All chemicals were of the best quality commercially available, and they have been used without further purification steps: AOT sodium salt (Fluka), *n*-heptane (Fluka), NH_4F (Fluka), $Mn(CH_3COO)_2$ (Fluka), acetone (Merck). The used water was ion-exchanged and active-coal filtered.

2.2. Synthesis. *The conversion of the AOT sodium salt* into other salts has been described, e.g., by Kitahara.[18] AOT−NH₄ was prepared by the metathesis reaction of methanolic AOT−Na and aqueous NH_4Cl solution. The efficiency of the procedure was verified by flame spectroscopy. The sodium content was less than 10^{-4} wt %.

The microemulsion systems (Table 2) were based on *n*-heptane/AOT−NH₄ as organic dispersion medium/surfactant mixture in a weight ratio of 1.2. We did not add any cosurfactant. After adding the aqueous salt solution (containing $Mn(CH_3COO)_2$ or NH_4F, respectively), the mixtures were stirred until water-clear appearance indicates the formation of a microemulsion. The concentrations of the $MnAc_2$ solutions were chosen in correct stoichiometry to the NH_4F solutions. The

Table 2. Synthesis Parameters

sample name	concn of the NH₄F solution [mol/(kg H₂O)]	synthesis temperature	Δt_{M-C} [min]	wt % of aqueous phase
A	3.0	rt	1	10
B	3.0	rt	**4**	10
C	3.0	rt	**30**	10
D	3.0	rt	1	**5**
E	3.0	**0 °C**	1	10
F	**1.83**	rt	1	**9.65**
G	**2.0**	rt	**8**	10

Table 3. Varied Synthesis Parameters To Investigate the Influence of Salt Content

sample name	*n*-heptane/ AOT−NH₄ mixture [g]	salt content [g]	water content [g]
A, B, C, E	60	**0.667 g of NH₄F**	6.004
A, B, C, E	60	**1.471 g of MnAc₂**	5.196
F	60	**0.407 g of NH₄F**	6.004
F	60	**0.897 g of MnAc₂**	5.196

absolute contents of the aqueous phase (wt %) of the two microemulsions to be mixed, containing NH_4F and $MnAc_2$, were identical in the case of the experiments A, B, C, D, and E, listed in Table 3. To investigate the influence of the salt content on the crystallite size, only the absolute amount of salt was varied, keeping the content of AOT−NH₄, *n*-heptane, and water constant (sample F compared with sample A, see Table 3).

In order to precipitate NH_4MnF_3, equal amounts of both microemulsions were mixed under vigorous stirring. The result was an optically transparent sol, i.e., a colloidal dispersion of nanocrystalline NH_4MnF_3 in *n*-heptane/H_2O, to a certain extent stabilized by AOT.

The coagulation of the sols was performed with acetone (600 mL per 100 mL of microemulsion) by adding the mixed microemulsions to the acetone under vigorous stirring. In this step also the soluted salt NH_4Ac and the soluted part of NH_4MnF_3 were precipitated. The period of time between the mixing of the microemulsions and the coagulating process, Δt_{M-C}, was varied between 1 and 30 min (Table 2). The result is the raw product of *n*-NH_4MnF_3, containing the byproducts NH_4Ac and adsorbed surfactant.

The purification of the raw product was realized by boiling it repeatedly in acetone. The acetamide solubilized in acetone was removed each time by decantation. Finally the raw material contaminated with adsorbed AOT was purified by Soxhlet extraction with acetone for 20 h. The result was a fine white powder.

The size control of the resulting nanocrystalline NH_4MnF_3 was performed by varying Δt_{M-C} (the period of time between the mixing of the microemulsions and the coagulation with acetone), the content of aqueous phase, the synthesis temperature, and the salt content.

The synthesis parameters are listed in Tables 2 and 3. The varied parameters are indicated. The abbreviation rt denotes room temperature.

2.3. Characterization. *TEM micrographs* were recorded using a JEOL 200CX transmission electron microscope.

X-ray diffractograms of the powders were measured at room temperature on a Siemens D 500 diffractometer. Radiation was secondarily monochromated Cu Kα, the sampling conditions were a scan in steps of 0.02° (2θ) with a step time of 2 s. The resulting diffraction pattern was compared to the JCPDS file system.

2.4. Determination of the Crystallite Size Distribution by X-ray Line Shape Analysis. From the broadening of X-ray diffraction peaks or, more precisely, from the line shape of these peaks, the crystallite size can be determined. A common procedure is the Warren/Averbach method[19] which

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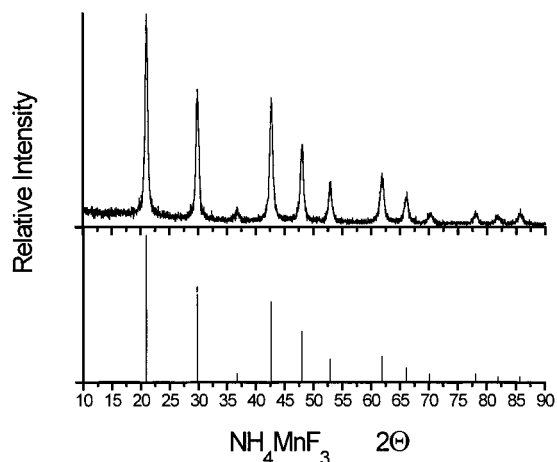(19) Warren, B. E.; Averbach, B. L. *J. Appl. Phys.* **1950**, *21*, 595.

Figure 1. XRD pattern of nano-NH_4MnF_3. Upper part: experimental diffractogramm. Lower part: diffraction peaks of NH_4MnF_3 according to the JCPDS file.

we use in a slightly modified version.[20,21] The primarily resulting size quantities are the volume and area weighted column lenghts, $\langle L \rangle_{vol}$ and $\langle L \rangle_{area}$. Thereby "column" means a column of unit cells in the crystallite perpendicular to the diffracting lattice planes. Henceforth we assume a spherical shape of the particles; for the central column of a sphere the column length equals the sphere diameter, but all other columns and therefore the average column length are smaller. Conversion formulas are due to Smith[22] and Krill and Birringer:[21]

$$\langle D \rangle_{area} = {}^3/_2 \langle L \rangle_{area} \qquad (1)$$

$$\langle D \rangle_{vol} = {}^4/_3 \langle L \rangle_{vol} \qquad (2)$$

Assuming a log normal distribution of the crystallite diameter D,

$$\langle D \rangle_{area} = \frac{1}{\sqrt{2\pi} D \ln \sigma} \exp \frac{-(\ln D - \ln \mu)^2}{2(\ln \sigma)^2} \qquad (3)$$

the median μ and the relative width σ of the size distribution of the crystallite diameter can be obtained by solving the following system of equations:

$$\langle D \rangle_{area} = \mu \exp({}^5/_2 \ln^2 \sigma) \qquad (4)$$

$$\langle D \rangle_{vol} = \mu \exp({}^7/_2 \ln^2 \sigma) \qquad (5)$$

Henceforth we use the short term "grain size" always for "volume-averaged particle diameter" and recommend this procedure for general use.

3. Results

3.1. Characterization of the Precipitates. Figure 1 shows the XRD pattern of a nanocrystalline NH_4MnF_3 sample with line broadening caused by the reduced size of the crystallites. TEM micrographs with two examples of size-modified NH_4MnF_3 crystallites are given in Figure 2. Both micrographs show agglomerates.
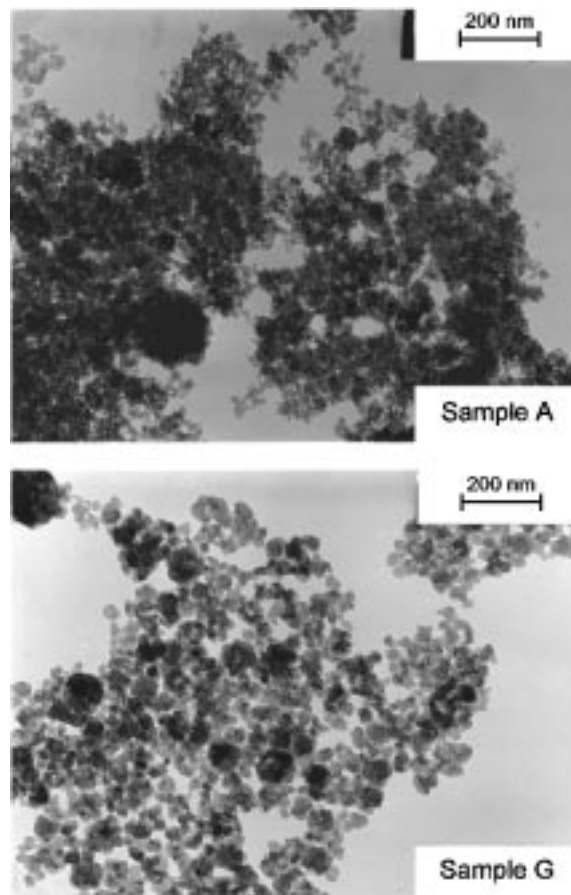
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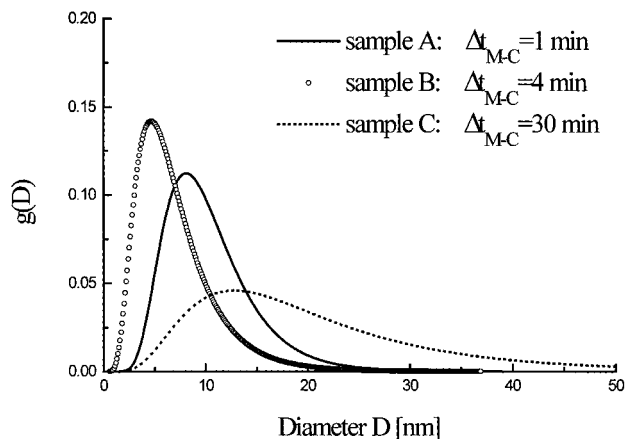(22) Smith, W. L. *J. Appl. Crystallogr.* **1976**, *9*, 187.

Figure 2. TEM micrographs of nano-NH_4MnF_3; a higher concentrated salt solution and a shorter time Δt_{M-C} leads to smaller crystallites (upper TEM micrograph).

Table 4. Grain Size and Grain Size Distribution of NH_4MnF_3 Resulting from Our ME Synthesis

sample	μ [nm]	σ	$\langle D_{vol} \rangle$ [nm]	max of distribution [nm]
A	9.5	1.50	17	8.0
B	6.1	1.69	16	4.5
C	17.8	1.78	56	13.0
D	5.4	1.53	11	4.5
E	7.8	1.53	15	6.5
F	19.9	1.32	27	18
G	20.9	1.46	35	18

The *relative* yields of the syntheses were 100 % (coagulation in acetone is linked with complete precipitation!). At best the *absolute* yield was 0.6 g of NH_4MnF_3 per 100 g of microemulsion (samples A, B, C, E).

3.2. Size Control. The results of the size-controlling experiments are given in Table 4 and illustrated by the crystallite size distributions shown in Figures 5–8.

The time Δt_{M-C} is the parameter with the most distinct influence on the resulting grain sizes of the precipitates (see Figure 3). In case of the synthesis of the samples A and B the microemulsion mixture was clear until the coagulation, whereas the ME of sample C became milky white due to the agglomeration of the formed particles. A time Δt_{M-C} of 30 min in the case of sample C leads to a wide distribution with larger crystallites than those of samples A and B. The amazing fact that the grain size of sample B (coagulated after 4 min) is smaller than the size of sample A (coagulated after 1 min) is discussed in 4.2.

The grain size is also effected by *the content of the aqueous phase*. The decrease of the amount of aqueous

Figure 3. Influence of the time between mixing and coagulation, Δt_{M-C}, on the crystallite size of nanocrystalline NH_4MnF_3.
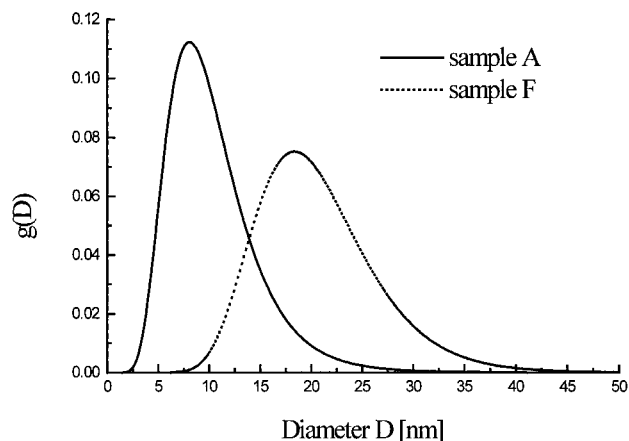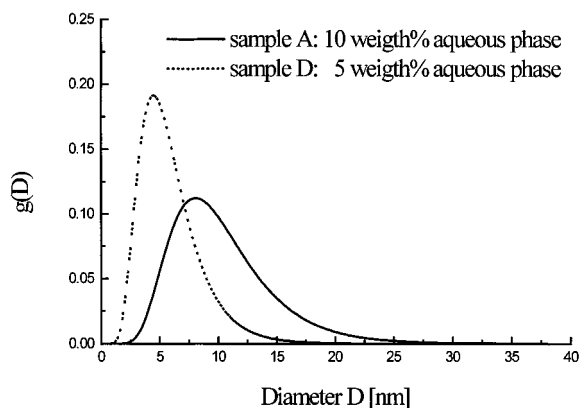

Figure 4. Influence of the content of aqueous phase on the crystallite size distribution of nano-NH_4MnF_3.
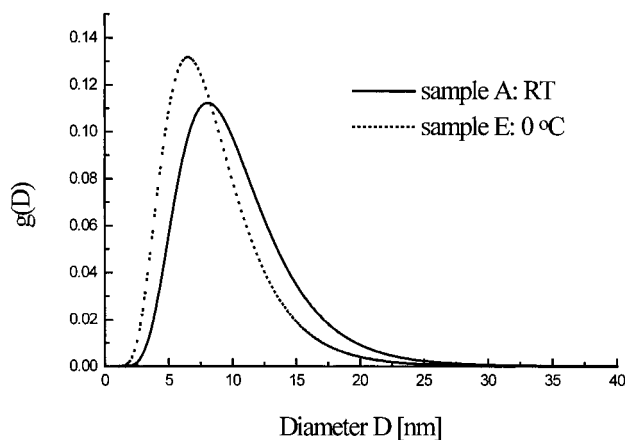

Figure 5. Influence of the synthesis temperature on the crystallite size distribution of nano-NH_4MnF_3.

phase in the microemulsion from 10 to 5 wt % (sample A and sample D) leads to a decrease of the grain size and a narrower grain size distribution, see Figure 4.

The synthesis temperature (see Figure 5) is only of minor influence. At the lower temperature of 0 °C the produced grains are smaller than those precipitated at room temperature.

Starting from a lower *salt content* of the ME (sample F compared with sample A, see Figure 6), the crystallites exhibit larger grain sizes than those produced by a higher amount of salt in the microemulsion systems. Furthermore, the size distribution is narrower in the case of sample A.

Figure 6. The influence of the salt content on the crystallite size distribution of nano-NH_4MnF_3.

4. Discussion

4.1. The Efficiency of the Synthesis Route. The employment of ammonium and acetate salts in w/o-microemulsions with AOT−NH₄ as surfactant enables the production of pure nanocrystalline substances via precipitation, in our case NH_4MnF_3 according to:

$$3NH_4F + MnAc_2 \rightarrow NH_4Mn\,F_3 + 2NH_4\,Ac$$

In the course of the subsequent coagulation in a surplus of acetone, the water is withdrawn by acetone, resulting in NH_4Ac precipitation. This undesired byproduct, however, can conveniently and indulgently be decomposed and completely removed by boiling the raw product in acetone:

$$CH_3COONH_4 \rightarrow CH_3CONH_2 + H_2O$$
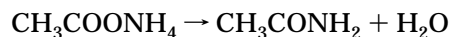
Both acetamide and water are very soluble in acetone; therefore contamination of the product by counterions can be avoided.

The second advantage of the surfactant AOT−NH₄ is the high solubility of NH₄F and NH₄Ac in water, in contrast to the corresponding Na salts. This allows one to work with comparatively high salt concentrations in the microemulsions, resulting in a correspondingly high yield. Actually, we succeeded in stabilizing a 3.0 M NH₄F solution in a microemulsion up to 15 wt % of aqueous phase content.

We assume that our ME-mediated ammonium acetate precipitation route is applicable to the production of not only nanocrystalline NH_4MnF_3 but also of a number of other nanocrystalline salts, with low impurity content and large yield. We ourselves have meanwhile prepared n-MnS, n-Fe₃O₄, and n-LiF using this synthesis route.

4.2. Size Control. The special and inconvenient feature of our preparation route is the fast growth process of the particles which has not been observed in other works[9−14] where the primary particles formed in the microemulsions are colloidally stabilized by the surfactants and thus protected against agglomeration. Hou and Shah,[11] e.g., studied the kinetics of the agglomeration of n-AgCl sols and found that within 250 min the particles grow only by a few nanometers, whereas we observe a growth orders of magnitude faster and an appreciable broadening of the size distribution after 30 min. We attribute this agglomeration process

to a fast intermicellar exchange supported by the comparatively large solubility of NH_4MnF_3. Under the condition of vigorous stirring, time constants of $1-2$ ms[11] and 60 ms[23] have been reported in the literature. In the latter case the kinetics of intermicellar exchange was measured by means of a continuous flow method.[23]

Δt_{M-C}, the period of time between mixing and coagulation has a favorable influence on the particle size and size distribution. An interesting aspect of our synthesis is the observed sequence of decreasing and then increasing particle sizes with time. This might be due to the fast intermicellar exchange: The NH_4F aqueous solution of the first initial ME and the $MnAc_2$ aqueous solution of the second initial ME are quickly mixed, and NH_4MnF_3 precipitates, as desired, in the confined space of the micelles (nanoreactors). But as a consequence of the fast intermicellar exchange, the primary NH_4MnF_3 nanoparticles probably exhibit Oswald ripening, i.e., the larger crystals grow at the expense of the smaller ones. This growth process, of course, is not desired and has to be stopped by pouring the ME system into acetone where the colloidal nanoparticles coagulate. Therefore, in order to use the uniform space confinement of the microemulsion droplets for the preparation of nanocrystalline precipitates, one has to compromise: the time between mixing and coagulation, Δt_{M-C}, has to be as long as necessary for the precipitation but as short as possible in order to minimize Oswald ripening. This could explain the sequence of increasing grain sizes of samples B, G, and C with increasing Δt_{M-C}. We assign the instability of the formed sol indicated by the milky white color of the ME of sample C and the observed rapid agglomeration and crystal growth process to the relative high solubility of the NH_4MnF_3 salt which favors the crystallite growth. Indeed the solubility of the trifluoride is several orders of magnitude higher than that of the precipitates produced up to now via ME (given in Table 1).

On the other hand, if Δt_{M-C} is too short (1 min), precipitation in the ME droplet does not seem to be finished, and the NH_4MnF_3 still soluted in the aqueous phase might precipitate mainly in the acetone, without the effect of space confinement. This is indicated by the fact that a larger particle size results for sample A compared to sample B. A reasonable compromise seems to be $\Delta t_{M-C} = 4$ min; in this way we yielded our smallest n-NH_4MnF_3 particles.

The influence of the aqueous phase content could be explained as follows. To reduce the aqueous phase content means to reduce the total volume of the micelles (i.e., the sum of the volumes of all micelles contained in the ME system). Presently it is not clear whether the decrease of the amount of aqueous phase influences the size or the number of the micelles. Corresponding light scattering experiments are in progress now. One possible explanation for the reduced particle size in the case of a lower total micelle volume could be a smaller intermicellar exchange rate during the precipitation time and a smaller probability for the resulting particles to come into contact with each other. The consequence would be a slowing down of the agglomeration and growth process.

The influence of the synthesis temperature can possibly be explained by the temperature dependence of the Brownian motion. We assume that a decrease of the ME temperature effects a decrease of the intermicellar exchange by slowing down the Brownian motion. Additionally, the agglomeration process is retarded. The effect of the temperature-depending solubility of NH_4MnF_3 on the crystallite size was not investigated in the present work.

The influence of the salt content on the particle size could be the increase in interfacial rigidity with increasing salinity as observed by Leung and Shah.[24] At higher interfacial rigidity the intermicellar exchange is slowed down. This could explain the larger grain size of sample F compared to sample A.

5. Summary

In a ME system of AOT$-NH_4$/*n*-heptane/aqueous salt solution it is possible to produce nanoscale NH_4MnF_3 crystallites and to control the size of the resulting product by varying the following parameters: the time Δt_{M-C}, the aqueous phase content, the synthesis temperature, and the salt content.

The special feature of our ME-mediated ammonium acetate precipitation route is the indulgent decomposition and removal of the counterion contamination consisting in NH_4Ac. Apart from n-NH_4MnF_3 this synthesis route might also be useful for the preparation of other new nanocrystalline materials; for instance, n-MnS, n-Fe_3O_4, and n-LiF could already be prepared by us. Therefore to our mind this synthesis route exhibits a certain general validity.

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