# Formation and structure of cubic particles of sodium magnesium fluoride (neighborite)

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**Abstract**

Uniform cubic particles of neighborite ($NaMgF_3$) were prepared by mixing solutions of magnesium chloride and sodium fluoride, followed by aging for extended periods of time (up to 3 h). Such particles could be obtained directly either by using sodium fluoride in sufficient excess, or by first producing spherical particles of magnesium fluoride and converting them into neighborite cubes by admixing sodium fluoride. It was shown that both $MgF_2$ and $NaMgF_3$ particles so prepared are polycrystalline and that in both procedures to form neighborite a two stage reaction takes place. In the first stage nanosize subunits of $MgF_2$ are formed, which are subsequently converted in the presence of excess sodium fluoride to neighborite crystallites. The latter are then reorganized into larger subunits that constitute colloidal cubes.
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## 1. Introduction

Over the past several decades a large number of dispersions, consisting of uniform particles of simple and composite nature, have been reported in the literature [1–3]. In principle, the most versatile method to produce such dispersions is by precipitation in solutions. The latter process may involve different mechanisms of formation, such as polymerization of solutes in liquid media [4,5], diffusional growth following the nucleation stage [6,7], or aggregation of preformed nanosize precursors [4]. One of the challenges in fine particle science is to predict the shape of the particles obtained by precipitation. This task was achieved only in a limited number of cases. For example, amorphous spherical particles result—as a rule—by the polymerization of constituent solutes such as in the hydrolysis of multivalent cations [4,5]. Furthermore, in some cases diffusion processes may produce uniform crystals of the habit characteristic of a given mineral. Particularly intriguing are the situations where uniform colloidal particles are formed by aggregation of nanosize precursors, which can yield particles of different shapes including spheres. It is noteworthy that the aggregation process has been proven to be more common than originally anticipated. A model was proposed that explains the size selection of uniform polycrystalline spheres obtained by nucleation [8] and tested on examples of gold and cadmium sulfide [9]. In contrast, there are no models available to explain the formation of particles with shapes other than spherical. The task is more difficult when dispersed solids of the same chemical composition could be produced in different shapes just by varying the concentrations of the reactants. It was shown at least in the case of hematite ($\alpha$-$Fe_2O_3$) [10] that the final particles' crystal habit was related to the shape of the nanosize precursors [11], but no such relationship was found in other systems [12].

In order to develop some understanding of the shape produced by such a complex aggregation mechanism, it is necessary to carefully examine the formation of dispersions of particles of a given shape. It is also essential that such uniform particles be of simple chemical composition in order to avoid difficulties that occur when precipitation takes place in solutions containing multiple solute complexes. In this study the choice was made to explore in some detail the formation of monodispersed cubes of $NaMgF_3$ (neighborite). In a prelimi-

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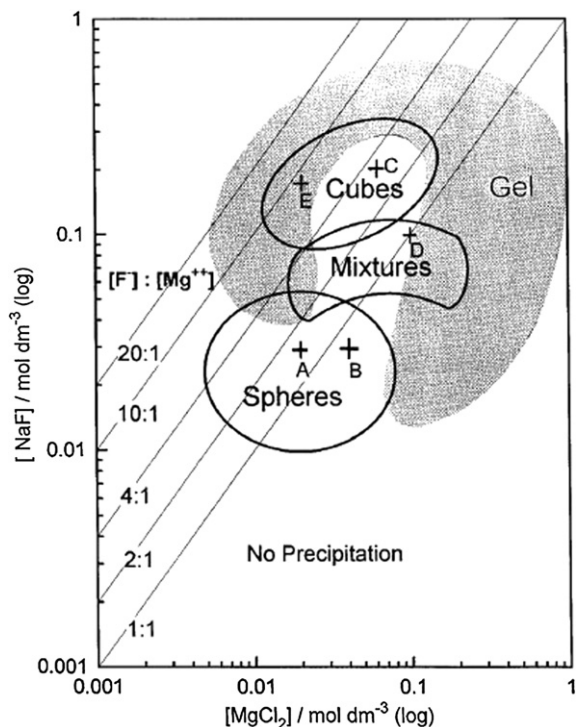*E-mail address:* matiegon@clarkson.edu (E. Matijević).

Fig. 1. Composition domains of precipitates formed by mixing solutions of different concentrations of NaF and $MgF_2$, aged at 80 °C for 3 h [13].

nary study [13], it was shown that such particles can be obtained by mixing solutions of NaF and $MgCl_2$, and that their composition and shape depended on the reactant concentrations, as illustrated in Fig. 1. It was also demonstrated that the resulting solids consisted of nanosize subunits. However, the formation of the cubes proceeds through a more complex mechanism than what appeared to be the case, as elucidated in this study. The new experiments provide strong evidence that the generation of cubes occurs in two stages. During the first stage, nanosize crystallites of $MgF_2$ are formed, which are then transformed into primary subunits of $NaMgF_3$, the building blocks for micrometer size cubic particles. While being a very good model for studying the particle shape factor, the preparation of finely dispersed neighborite is of additional interest, because of its use as a perfect latent thermal storage material [14,15].

## 2. Experimental

### 2.1. Materials and characterizations

Sodium fluoride and magnesium chloride (Fisher) of highest purity grade were used for particle preparation. The resulting solids were inspected by transmission (TEM JEM-2010) and scanning (FESEM JEOL-7400) electron microscopes. The structure of the particles was evaluated by electron diffraction (JEM-2010) and X-ray diffraction (XRD Bruker-AXS D8 Focus), while the chemical composition of the solids was qualitatively assessed by energy dispersive spectroscopy (EDS JEOL JSM-6300). To prepare samples for TEM, FESEM and EDS, a drop of the suspension was placed on a grid or a stud and the supernatant liquid was removed with a capillary after the par-

ticles were allowed to settle. As needed, the specimens were evaluated either uncoated or coated with gold. The size distribution of the dispersions was determined by laser diffraction (Malvern Mastersizer 2000 with HYDRO 2000 accessories). For this purpose, a sufficient volume of dispersion was added into the instrument's chamber to provide the optimum particle concentration and ultrasonication was applied for 5 min. A thermostated water bath was used for preheating and aging of solutions.

### 2.2. Preparation method

Colloidal particles used in this study were prepared by mixing aqueous solutions of NaF and $MgCl_2$. More specifically, the reactant solutions were preheated to 80 °C in a water bath and rapidly combined in different predetermined volume ratios. A white precipitate appeared essentially immediately after combining the reactant solutions and the particles settled within ∼30 min. However, on agitation the sediment readily redispersed. The dispersions were then aged at the same temperature for three more hours, while samples were periodically removed with a pipette for particles size, internal structure, morphology, and chemical composition analysis. After aging, the resulting solids were separated by filtration, washed repeatedly with water, and dried in vacuum. A number of experiments showed that the methods of cooling and drying particles had no noticeable effect on their shape and size. Also, replacing magnesium chloride with magnesium acetate had little effect on particle properties.

Additional experiments were carried out to test the effects of precipitate solubility by changing the solvent and of the reaction temperature. The former was studied by partially replacing the water with ethanol into the reactant solutions while keeping the rest of the conditions the same as in experiment C, Table 2. The effect of the temperature was investigated by running reactions in the same conditions at 25 and 40 °C.

## 3. Results

It was shown earlier [13] that, depending on reactant concentrations, the resulting particles consisted of either magnesium fluoride ($MgF_2$) or neighborite ($NaMgF_3$).

### 3.1. Formation of $MgF_2$

This study confirmed that in the absence of a large excess of NaF (samples A and B in Table 1) uniform spherical particles are formed (Fig. 2) indeed, their modal size being larger at higher reactant concentrations. Samples taken approximately every 10–15 min during a subsequent aging period of one hour showed that spheres grow slightly with time. The X-ray diffraction pattern of the solids is characteristic of $MgF_2$ (Fig. 3). Furthermore, the XRD data confirmed the composite internal structure of those particles, consisting of subunits of 5–15 nm in diameter, as derived by the Scherrer method [16]. The chemical composition was corroborated by EDX analysis, which showed only Mg and F peaks.

Table 1

| Sample | Stock solutions | | | | Concentration after mixing | | Results |
|---|---|---|---|---|---|---|---|
| | NaF | | $MgCl_2$ | | NaF | $MgCl_2$ | |
| | $C$ (mol dm$^{-3}$) | $V$ (cm$^{-3}$) | $C$ (mol dm$^{-3}$) | $V$ (cm$^{-3}$) | $C$ (mol dm$^{-3}$) | $C$ (mol dm$^{-3}$) | |
| A | 0.05 | 10 | 0.05 | 10 | 0.025 | 0.025 | Fig. 2a |
| B | 0.1 | 10 | 0.05 | 10 | 0.05 | 0.025 | Fig. 2b |

Table 2

| Sample temperature | Stock solutions | | | | Results |
|---|---|---|---|---|---|
| | NaF | | $MgCl_2$ | | |
| | $C$ (mol dm$^{-3}$) | $V$ (cm$^{-3}$) | $C$ (mol dm$^{-3}$) | $V$ (cm$^{-3}$) | |
| C, 80 °C | 0.2 | 100 | 0.2 | 10 | Fig. 4b |
| D, 40 °C | 0.2 | 100 | 0.2 | 10 | Fig. 7a |
| E, 25 °C | 0.2 | 100 | 0.2 | 10 | Fig. 7b |
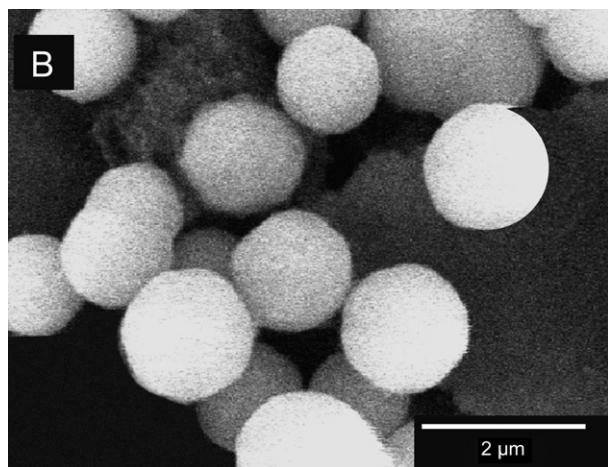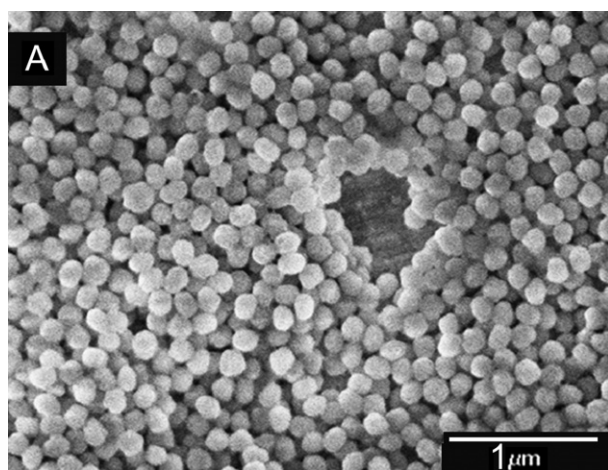


Fig. 2. MgF$_2$ spheroidal particles prepared under conditions given in Table 1: (A) sample A, (B) sample B.



Fig. 3. XRD diffraction pattern of spheroidal polycrystalline MgF$_2$ particles (sample B, Table 1).



Fig. 4. The effect of time on the formation of NaMgF$_3$ particles at 80 °C (sample C, Table 2): (A) aged for 10 min and (B) aged for 3 h.

## 3.2. Formation of NaMgF$_3$ (neighborite)

When a large excess of NaF was used (sample C, Table 2) the resulting particles clearly displayed the cubic shape (Fig. 4). During the early stages of the reaction the solids already ap-
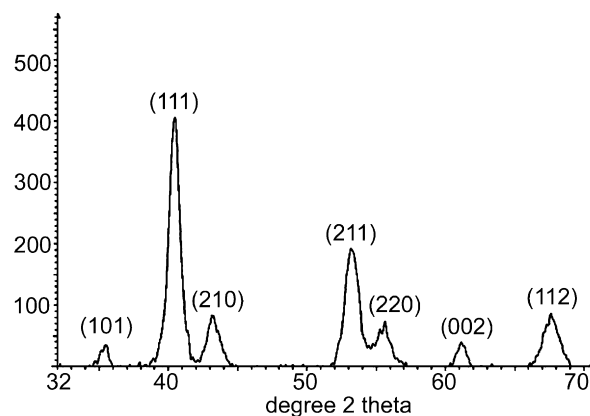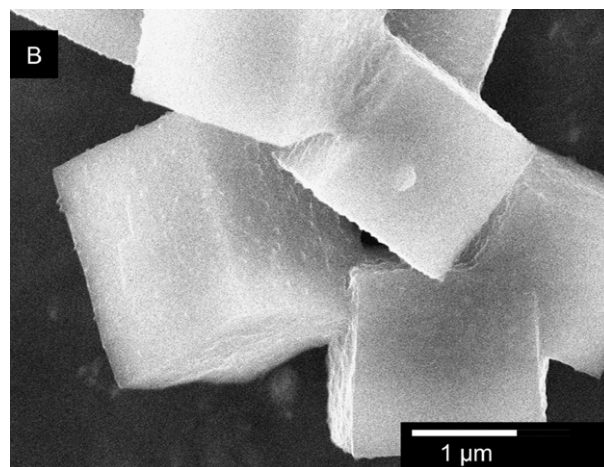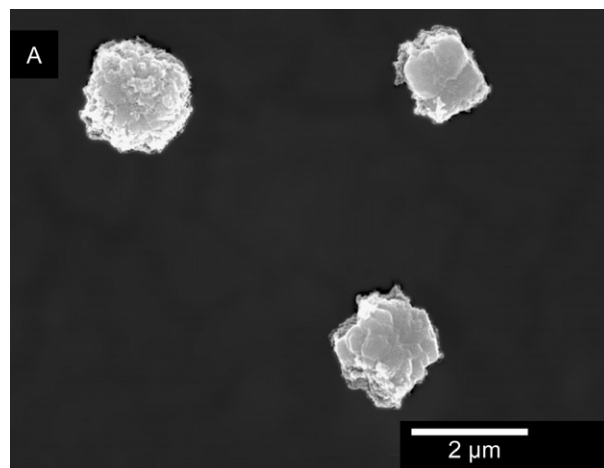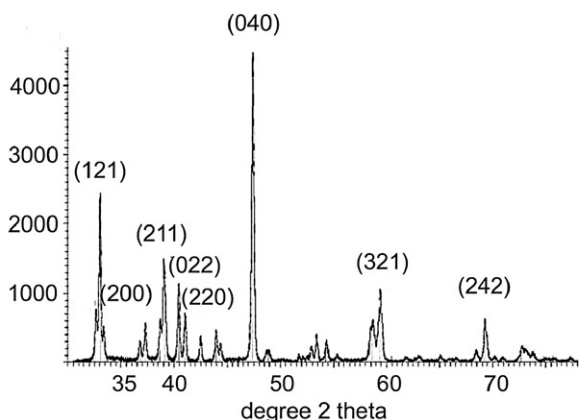
Fig. 5. XRD diffraction pattern of cubic particles as NaMgF$_3$ polycrystalline (sample C, Table 2).
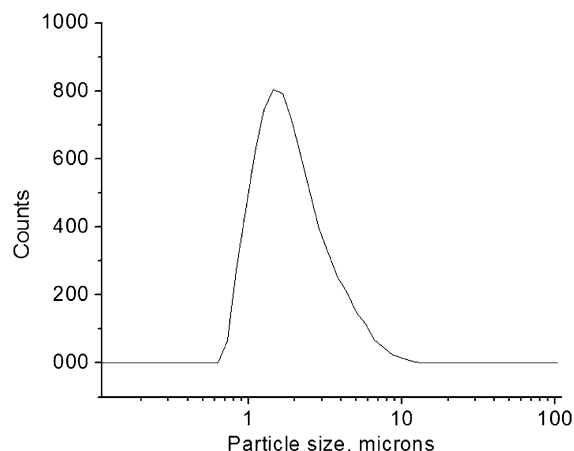


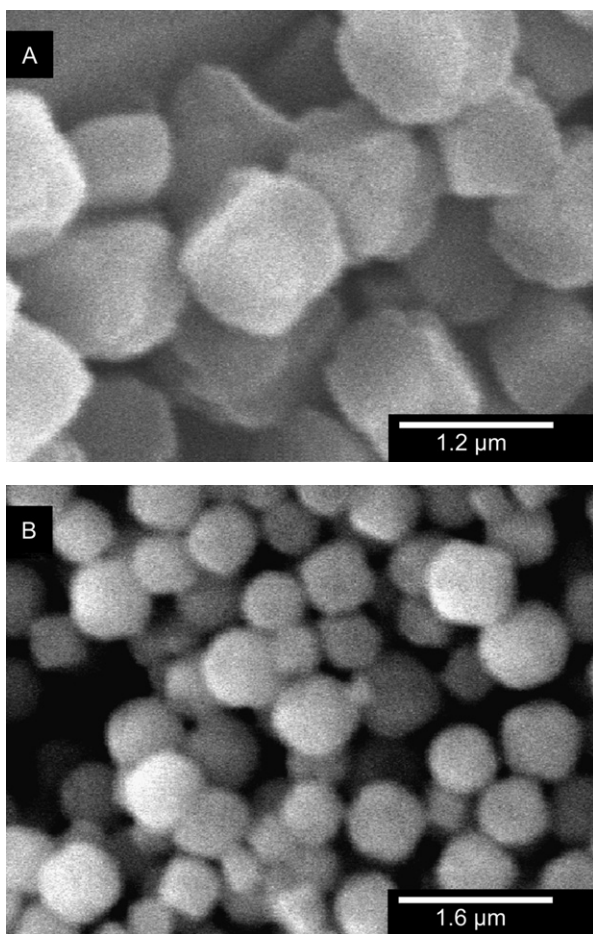Fig. 6. Size distribution of NaMgF$_3$ cubic particles (sample C, Table 2).



Fig. 7. The effect of temperature on the formation of NaMgF$_3$ particles: (A) the system showed in Fig. 4 aged at 40 °C and (B) at 25 °C (samples D and E, Table 2).



Fig. 8. The effect of added ethanol on the shape of particles NaMgF$_3$: (A) in sample C (Table 2) 30% (by volume) of water was replaced with ethanol and (B) 50 cm$^3$ of ethanol was added to the dispersion of sample C and continued aging at 80 °C for an hour.

peared as cubes, although their surface was rough and the edges poorly defined (Fig. 4A). After aging the solids for three more hours, the dispersed solids became cubes of approximately 1.5 μm with smooth surface and well defined edges (Fig. 4B).

The X-ray powder diffraction analysis identified the solid phase as neighborite (Fig. 5) and revealed that the large particles
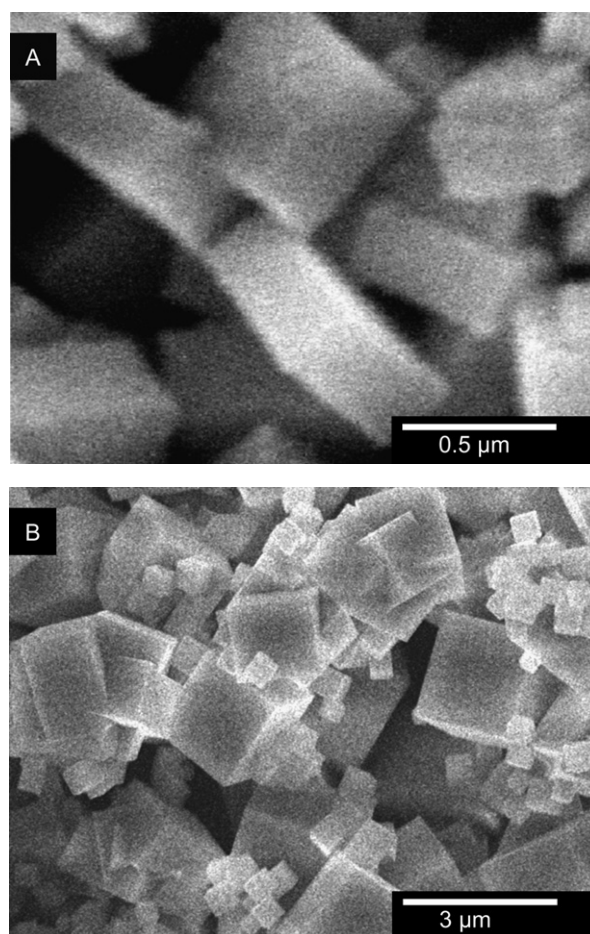
are also aggregates consisting of nanosize subunits. The size of the latter was estimated by the Scherrer method to be 50–100 nm.

The size of neighborite polycrystalline cubes, evaluated by laser diffraction method, ranged between 0.8–4 μm (Fig. 6).

However, the method dos not exclude some aggregates. The sizing of particles from electron micrographs showed them to have an edge 0.8–2 µm.

Additional experiments were carried out using the same reactant concentrations at two lower temperatures, i.e. at 25 and 40 °C. The representative FESEM micrographs are given in Figs. 7A and 7B.

While the precipitation proceeded as fast as at 80 °C, the morphology of the particles was affected by temperature. At 40 °C the cubes became less pronounced with rounded corners, while at 25 °C the particles were nearly spheroidal. However, X-ray pattern of all these samples was the same as of one shown in Fig. 5.

As one would expect, changing the solubility of the reactants and of the final product should have an effect on the properties of the resulting particles. To evaluate this effect, mixtures of water and ethanol were used instead of pure water to dissolve the two salts (the solubility of $MaCl_2$ and NaF decreases by one order of magnitude in pure ethanol relatively to water [17]). Fig. 8A shows that, when 30% (by volume) of water was substituted with ethanol, at the experimental conditions of sample C, Table 2, the shape of the prepared particles was still very regular but not cubic. The effect of solubility was also evident when sample C was first prepared, and then 50 cm$^3$ of ethanol were added. In this case, secondary precipitation of $NaMgF_3$

particles occurred, solids were of cubic shape, but much smaller size as illustrated in Fig. 8B.

### 3.2.1. Structural characterization

While X-ray diffraction of cubic neighborite particles clearly indicated their composite nature, electron microscopic and etching studies were carried out to substantiate and identify the subunit constituents. It was noted that exposing cubes in the TEM chamber with a narrow (in comparison to the particle's size) high energy (200 keV) beam caused slow evaporation of matter from their surface. Fig. 9A compares two cubes: on the left side is seen the effect of the electron beam, while on the right side no radiation was applied. The light color area in Fig. 9B displays the part of the particle surface exposed to the electron beam for approximately one minute. Individual subunits became visible by applying a wider beam and longer exposure to the entire surface of the cube (Fig. 9C). The size of these subunits (50–100 nm) estimated on the enlarged image (Fig. 9D) is consistent with the value obtained from X-ray diffraction data.

## 4. Discussions

Earlier studies have shown that the nature of the products obtained by mixing solutions of NaF and $MgCl_2$ depended in
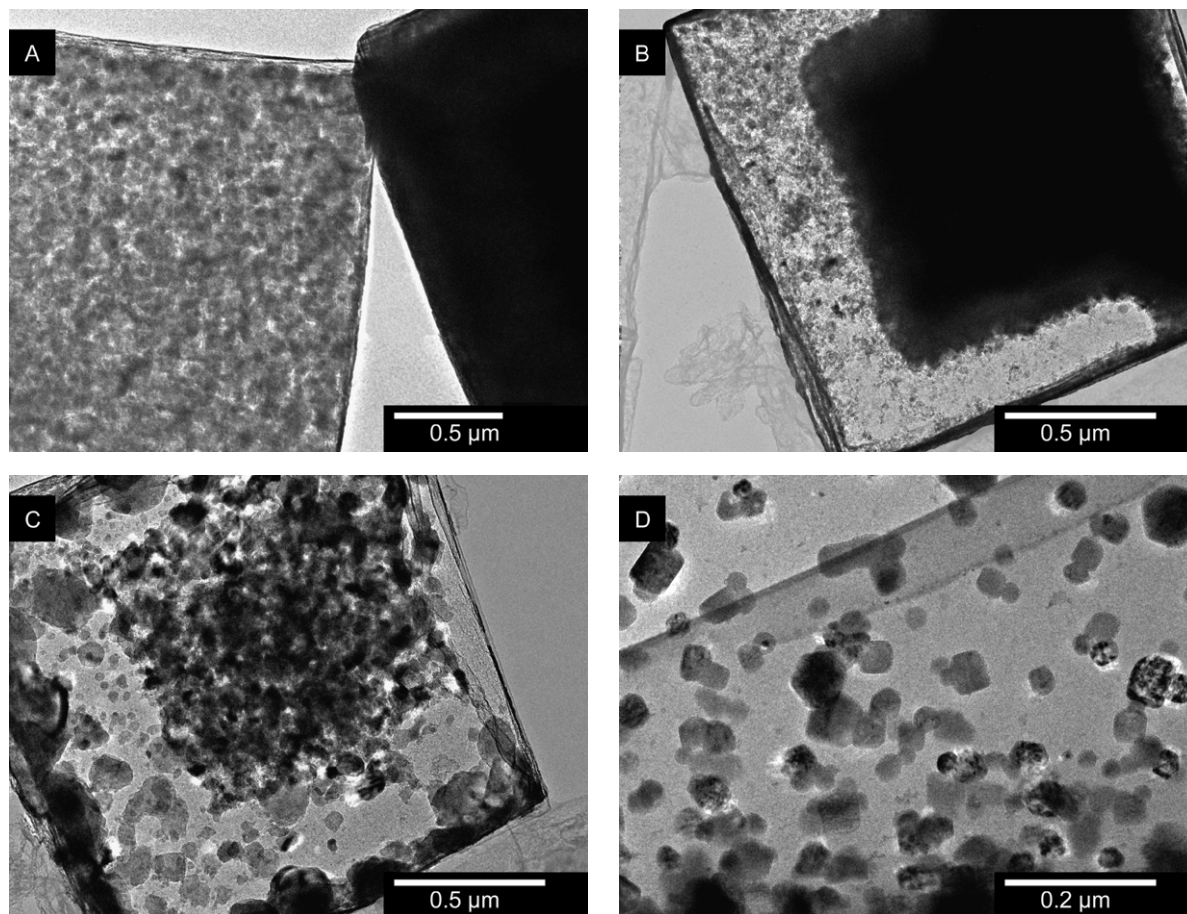


Fig. 9. Effect of electron beam radiation on $NaMgF_3$ cubic particles: (A) left: irradiated with 200 keV beam for ∼1 min and right: with no radiation. (B) Selected area of one particle exposed to the beam for ∼1 min, (C) entire area was exposed for ∼2 min, and (D) enlarged image of (C).
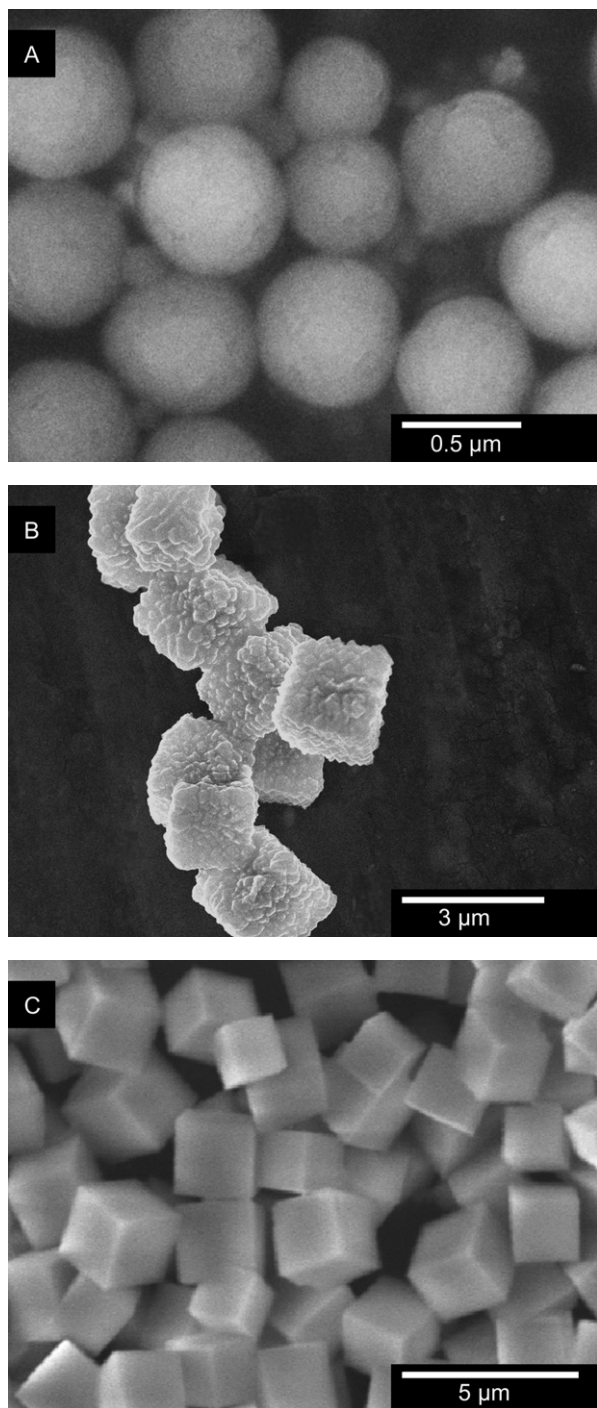
Fig. 10. Transformation of $MgF_2$ to $NaMgF_3$. (A) SEM of $MgF_2$ particles sample B. (B) To the dispersion shown in (A) additional NaF was added and aged for ∼2 h. (C) Same as (B) after continues aging at 80 °C for 5 h.

a sensitive way on the concentrations of the reactants as illustrated in Fig. 1. This finding did not offer an explanation regarding the mechanism by which cubic particles of neighborite were generated. The present study indicates that their formation proceeds through a two-stage process. At appropriate concentrations, spheres of $MgF_2$ are precipitated, which retained the

shape on aging. However, at sufficient excess of NaF, the $MgF_2$ particles still precipitate uniformly, but are then converted into $NaMgF_3$ cubes. During this process the sodium fluoride is incorporated into the crystalline lattice of the $MgF_2$ subunits causing a phase transformation and a change in the spatial arrangement of ions. This mechanism is supported by the enthalpy of formation data at 298 K, which are −1124 kJ/mol for $MgF_2$ [18], and −1716 kJ/mol for $NaMgF_3$ [19].

To test the feasibility of a two-stage process, supporting experiments were carried. At first, spheres of $MgF_2$ were prepared by the standard process (sample B, Table 1). To the dispersion of produced spherical particles (Fig. 10A) additional amount of NaF was added and the entire system was then kept at 80 °C for different periods of time. After 2 h cubic particles of rough surface were observed (Fig. 10B), which on further aging ended up as cubes of smooth surfaces (Fig. 10C). The solids had all the same characteristics as the dispersions prepared directly by mixing reactant solutions with sufficient excess of sodium fluoride.

When dispersions of spherical particles of $MgF_2$ were first aged for a longer period of time (3 h) and then reacted with admixed NaF, transformation into cubes also took place, but the process required much longer time. The resulting cubes were less regular in shape and of broader size distribution. Transformation of $MgF_2$ into neighborite also took longer time with lower concentration of added sodium fluoride. The entire transformation process into cubic particles must be affected by the composition of initial spheres of $MgF_2$ formed by aggregation of nanosize precursors (Fig. 10A). It would seem that on addition of NaF each of these nanosize subunits of $MgF_2$ crystallizes into neighborite (Fig. 10B), which at the elevated temperature is restructured into cubes. During this entire process the original subunits increase in size; while in the original spheres they are in the order of 10 nm, in the final cubes their average size is between 50–100 nm.

Uniform neighborite cubic particles (left/top) and magnesium fluoride spheroidal particles (right/bottom) formed in homogeneous solutions at 80 °C.

## Acknowledgment

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