



ELSEVIER

Journal of Crystal Growth 216 (2000) 407–412

JOURNAL OF **CRYSTAL
GROWTH**

www.elsevier.nl/locate/jcrysgro

Influence of magnetic field on sodium hexafluorosilicate synthesis

R. Chandrasekhar*

Particle Research Group, Science & Technology Research Centre, University of Hertfordshire, Hatfield, Herts AL10 9AB, UK

Received 19 October 1999; accepted 24 February 2000

Communicated by L.F. Schneemeyer

Abstract

Sodium hexafluorosilicate (SFS) crystals were synthesized by precipitation by the reaction of hydrofluorosilicic acid and sodium carbonate at a pH of 2.5 and 3.5 and a magnetic field of 5.5 T was applied immediately after precipitation for 45 min at 20°C. SEM, XRD and FTIR spectroscopy examined the crystals produced with and without a magnetic field. © 2000 Elsevier Science B.V. All rights reserved.

PACS: 81.10; 81.40; 61.66

Keywords: Solution growth; Sodium hexafluorosilicate; Magnetic field

1. Introduction

The purpose of this communication is to report on the pronounced effect of magnetic field during the preparation of SFS. The objective is to use SFS as an analogue of ice crystal (snow flakes) for light scattering measurements for climate modeling. Physicists have long recognized the remarkable beauty of snow crystals with simple geometrical shapes and intricate forms. They appear in a wide variety of shapes and forms that fall into four main classes: thin hexagonal plates, hexagonal columns, six pointed star combinations and hexagonal

needles. Their nature, origin and mode of action are of considerable importance in cloud physics and are matters of debate in climate modeling. Snow crystals have a refractive index of 1.31 in air at 20°C and it is difficult to reproduce them in the laboratory and equally difficult to carry out light scattering experiments in the laboratory. Therefore, it was decided to use an ice analogue. After considerable amount of screening of various crystallographic data base and refractive index of inorganic crystals one inorganic compound was identified to have a hexagonal shape and refractive index of 1.31 in air at 20°C and a very low birefringence (generally all hexagonal crystals have extremely low birefringence). The preparation of SFS was primitive and described in only one reference [1] and crystals produced are of different shapes. Hydrolysis of SFS in aqueous solution depends heavily on pH and

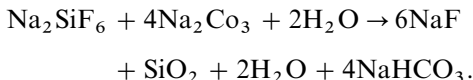
* Tel.: +44-1707-284656; fax +44-1707-282-185.

E-mail address: r.chandrasekhar@herts.ac.uk
(R. Chandrasekhar).

temperature. SFS decomposes to give sodium fluoride and silica. The hydrolysis can be written as



In the presence of sodium carbonate the following reaction takes place:



Therefore, we prepared this in an acidic medium to avoid decomposition at the time of preparation. We did not carry out preparation at each pH level and by product analysis as it is beyond the scope of our investigation. We have mentioned this only for the sake of readers who are unfamiliar with fluorosilicate preparation and wondering why a low pH was selected for our work. Given the tremendous emerging interest by climate modelers to study light scattering by ice crystals, we believe that developing an SFS crystal for such a system is an imperative step toward furthering this area and help climate physicist with a suitable product for light scattering measurements.

In this report we have examined the application of a magnetic field to prepare well-shaped crystals without defects. Some interesting phenomena related to magnetic field have been reported in biology and biophysics and in some chemical preparation. [2–5]. Mitrovic prepared manganese chloride and Rochelle salt by using a magnetic field. Manganese chloride is a paramagnetic compound and Rochelle salt is a salt of an organic acid with a complex structure [6,7]. There are other reports where an inorganic chemical such as barium chloride was prepared using a high magnetic field [8]. We examined what happens immediately after precipitation

of SFS when a high magnetic field is applied and examined the crystal shape, physical properties and compared the properties with a preparation without a field. A different route of synthesis was also followed other than in Ref. [1] to see whether we can produce a well shaped crystal without a magnetic field.

2. Experimental procedure

Experimental technique/set-up: (1) An NMR magnet of 5.5 T was used. The crystals were grown after precipitation and exposed to magnetic field. The crystal growth could not be observed with the sample inside the magnet, and the field could not be varied. This is our first paper and we hope to set up an electromagnet to vary the field fitted with an optical microscope to observe the changes with temperature during magnetization and crystal formation. (2) SFS crystals were prepared in distilled water and washed in distilled water throughout the experiments. Alternative preparations were made without a magnetic field using a mixture of sodium carbonate, triethanolamine and EDTA. The results are shown in Table 1 including the preparations using an applied magnetic field. The experiments were repeated five times. In all cases we obtained concordant results.

3. Procedure, materials and preparation

SFS was prepared by the gradual addition of a saturated solution of sodium carbonate (AR) grade to 200 ml of 20% hydrofluorosilicic acid AR grade ARCO Inc, NJ, USA at 20°C, till the slurry

Table 1
Synthesis condition

Sample	pH	Magnetized (M)/unmagnetized (UM)	Temperature°C of preparation/shape of crystal
1	2.5	UM	20 Surface blemish hexagonal, some odd
2	3.3	UM	20 Surface blemish hexagonal, some odd
3	3.3	M	20 Clearly hexagonal without surface blemish
4	3.3 ^a	UM	20 With blemish
5	3.3 ^a	M	20 Clearly hexagonal

^aEDTA, NaOH and triethanolamine combination.

pH was 2.5. The SFS formed was filtered washed with water and dried at 110°C for 1 h in an oven and marked as sample number 1 (no. 1). 0.5 g of this sample was poured into 200 ml of distilled water and this slurry showed a pH of 3.3. This was evaporated in a water bath and volume reduced to 100 ml (i.e. hydrolyzed). This sample was filtered and marked as A. The filtrate was evaporated and dried and marked as B.

In another set of experiments a sample was prepared and aged for 24 h at 20°C at a pH of 3.3, washed with water several times, dried in an oven at 110°C for 1 h (named as no. 2, blank). In another preparation a sample was prepared at a pH of 3.3 and immediately after precipitation was magnetized in an electromagnet designed for NMR analysis (5.5 T) for 45 min at 20°C and removed. The crystals were prepared as no. 2 and the sample marked as no. 3. A new chemical route other than no. 1 reference was followed; here the procedure was like no. 2 preparation except a 5% solution of NaOH (instead of sodium carbonate) was added with 10 ml of triethanolamine and 10 ml of 0.2 M EDTA till the pH was 3.3 and similar procedure to no. 2 was followed and crystals collected after drying were marked as no. 4. The reason for doing this is to see whether we get a better crystalline shape or some improvement in morphology without applying a magnetic field. A fifth sample was prepared similar to sample 4, but magnetized like no. 3 and marked as sample no. 5.

Throughout the precipitation of all the samples mentioned above, the pH was constant (monitored with a Philips pH meter). We noticed that long standing of a blank (similar to sample no. 2) resulted in extremely coarse, non-hexagonal large crystals of 50–100 μm unsuitable for light scattering studies. The preferred size range is between 1 and 10 μm crystals similar to snow flakes.

By the pH stated here during the preparation as 2.5 and 3.3 we mean the mother liquor contained an excess acid corresponding to the stoichiometric composition of SFS. The hydrolysis experiment also shows that we are keen to demonstrate samples we prepared containing neither free NaF nor SiO₂. This we have discussed under physical characterization. Each one of the samples was subjected to extensive SEM, XRD and FTIR analysis.

3.1. Scanning electron microscopy analysis (SEM)

A Cam Scan CS 44 was used for SEM examination. Micrograph of nos. 1, 2, and 4 sample showed no clear hexagonal-shaped crystals, some surface blemished hexagonal some odd-shaped lumps were obtained. However number 4 and 5 showed hexagonal crystals without any surface blemish and range from 1 to 10 μm in size (Figs. 1–5). The largest crystal looked like the smallest crystal as seen in Fig. 3. A number of samples were magnetized and they all have similar characteristics.

3.2. X-Ray diffraction analysis (XRD)

A Philips powder PW 1650/25 was used for XRD studies using Cu K_α, and Ni filter arrangement. XRD

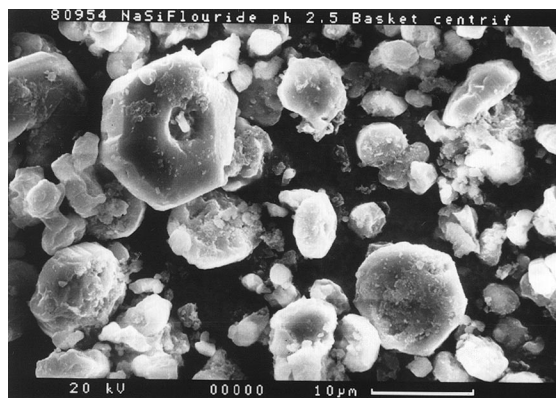


Fig. 1. SEM micrograph of sample No. 1 (pH 2.5).

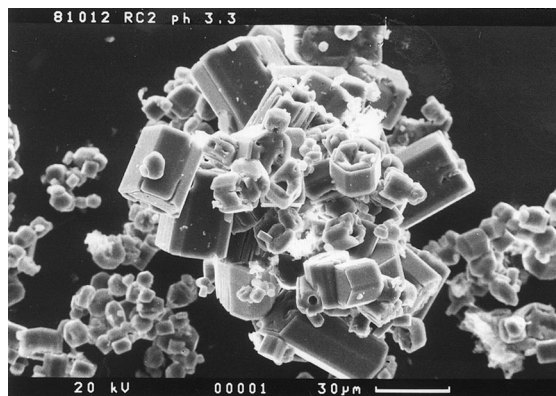


Fig. 2. SEM micrograph of sample No. 2 (pH 3.5).

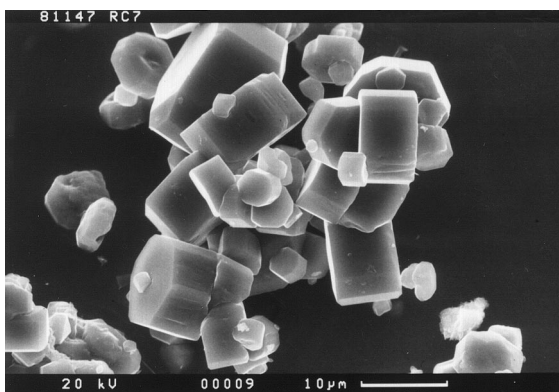


Fig. 3. SEM micrograph of sample No. 3 (pH 3.5 magnetized).

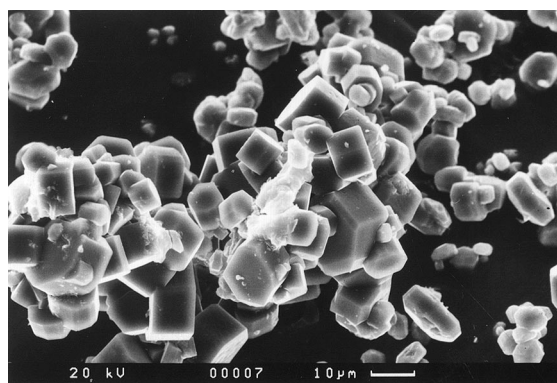


Fig. 5. SEM micrograph of sample No. 5 (EDTA method magnetized).

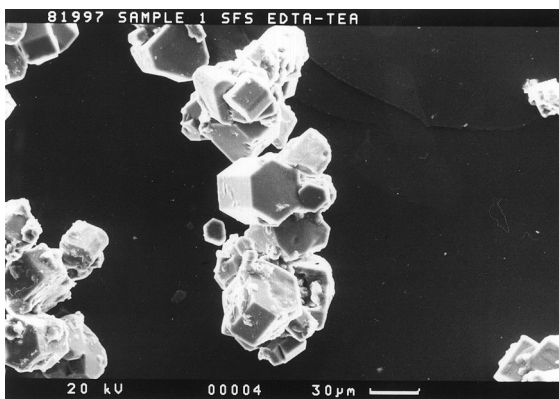


Fig. 4. SEM micrograph of sample No. 4 (EDTA method).

analysis was performed in all the samples. XRD analysis was also conducted on sodium fluoride and analar sodium hexafluorosilicate (ARCO). To verify the presence of sodium fluoride in the lab-prepared samples, various blends were prepared with SF:SFS analar in the ratios of 10:90, 20:80, 30:70, 40:60, 50:50. Diffractograms were obtained on the blended samples and the two were compared to see any contamination of fluoride. There was no evidence of fluoride in lab prepared samples or commercial sample. SFS's ASTM $2\theta^\circ$ values are 20, 21, 26.7, 29.5, 39.5 and 50.8, for NaF 38.5 and 56.0. The peak intensities are the same in all samples. There were no significant peaks for sodium fluoride. The most intense peak was 7% higher in the magnetized sample showing that the magnetized

sample is more crystalline than the unmagnetized lab and ARCO analar sample. It is also probable the peak intensity also may be due to the presence of some large crystals in the sample.

3.3. Fourier transform infra red analysis (FTIR)

FTIR analysis was carried out using a FTIR Galaxy 5000 instrument on magnetized and unmagnetized sample to see the presence of silica contamination in the samples. The samples were taken by the KBr method. The peak intensities are essentially unchanged. For the magnetized sample the peak intensities and wave numbers are similar to unmagnetized sample. There was no trace of silica in the spectrum. XRD is unlikely to show small traces of amorphous silica hence FTIR analysis on silica was conducted.

3.4. Fluoride analysis using a Fluoride electrode

A pH meter 610A, WPA Ltd, Lenton, Cambridge, was used for fluoride analysis. The analysis was carried out in our laboratory prepared samples, commercial Analar SFS sample, in blank and hydrolyzed samples. The indicator electrode is a fluoride-coated electrode cell; the reference electrode is a calomel electrode. The fluoride electrode measure the potential difference in a sample dispersed in water. The indicator electrode responds to an ion in solution by a change in potential as measured against the reference electrode. The indicator

electrode is the key component in this method of measurement to measure fluoride ion concentration. Before taking measurement the instrument was calibrated with a standard fluoride solution. The instrument is capable of measuring extremely low concentration of fluoride ion (i.e. 10 ppm). The method consists of dispersing 2 g of the sample in 100 ml distilled water and 10 ml of buffer (this is a mixed solution of NaOH 0.2 M solution, acetic acid (0.22 M), NaCl 1 M, CDTA (2 g/l), NaOCl 20 g/21 H₂O, pH adjusted with dil HCl and dil NaOH to a pH 5.5) and the potential difference is noticed for the magnetized, unmagnetized, commercial, blank and A, B samples. The potential difference was the same in all our samples indicating the absence of fluoride ion, in samples A and B, i.e. the absence of fluoride after hydrolysis. The experiments were repeated several times to test the magnetic memory.

4. Results and discussion

We have prepared SFS with and without a magnetic field; the magnetizing treatment of crystals in acid medium proved to be a better candidate than one treated without a magnetic field. Magnetic field application improves the crystallinity of the crystals as shown by morphology data. There was no fluoride or silica contamination in the prepared samples. Fluoride analysis has confirmed the absence of fluoride in unhydrolyzed and hydrolyzed samples. IR spectrum showed the absence of silica in the samples.

The actual mechanism by which a magnetic field affects the crystal growth is not well known, according to Mitrovic who carried out synthesis of manganese chloride and rochelle salt (a weak salt of an organic acid with a complicated structure like SFS/hydrofluorosilicic acid,) the ions of the salt which exists in solution would be subjected to considerable Lorentz force as they pass through the magnetic field. This may retard the growth by disrupting the regularity of the lattice. “The presence of magnetic field during crystal growth increases strain and correspondingly decreases the crystal growth. On the other hand, the increase in crystal growth may be explained by the fact that strain

built up during growth reaches some critical level after which it is released by dislocation formation” [6]. “Such a dislocation would play the role of a new sources of growth layers, and therefore the growth would increase” [6–11]. According to Ohagaki et al. who investigated barium chloride, “a change of strain due to magnetic field application during crystal growth change the energy of the bond, which in turn changes the liquid solid configuration at the interface. The radius of the nuclei also changes and in turn entail a new crystal formation and distribution due to the applied field” [8].

The Lorentz force or the field is the one, “where in each atom is considered as a magnetic dipole produces an external field and the sum of all the dipoles at a particular point would be a field from left to right tending to increase the alignment of the moment of the atom placed at that point, this Lorentz field is due to the north and south poles produced on the atom on the sides of that point. This force is also based on the ion’s moving electric charge and a force acts it on when it is in a magnetic field, the electrons will be deviated by an amount and in direction determined by the magnitude and direction of the magnetic field. It is possible that electrons with in a dual field environment experience the Lorentz force to its own electrical charge and electric field force associated with it”. It is also possible that magnetic fields prolong the electron residence time and this may leads to the probability of ion collisions and thus increased crystallization. This approach of Lorentz force and the use of a magnetron magnet applying a magnetic field during film formation is fully utilized in the thin film physics area for obtaining good density, separated crystals, clear crystal formation in single layer, multi-layer thin films [10]. However, in solution crystallization whether this Lorentz force is applicable during crystallization is unclear and this force will be very low. Other forces are strong enough to have any influence is uncertain. Mitrovic has however suggested a dominant two-dimensional nucleation when magnetic field is applied, and this may be a possibility, then Lorentz forces are unlikely to have any influence [6,11]. To date, there are no convincing literature references on magnetic effects in solution crystallization, but as mentioned previously, a number of new crystals have been

produced using a high magnetic field [8]. According to a recent paper by Madsen magnetic field increases crystallization, he claims it is a proton transfer from weak acids to water and orientation of proton spin [12]. However, he used a small magnetic field (0.27 T) and the orientation effect would be very small and this explanation is also puzzling. We consider and propose that orientation of large molecules (similar to needle-like viruses) by *large* magnetic fields, where the orientation is the result of the diamagnetic movement of these molecules.

5. Conclusion

We synthesized SFS in acid medium with and without a magnetic field. The application of a large magnetic field offered a better morphology than one without a field application. There is no evidence of silica or fluoride in our samples. Magnetizing the samples at 5.5 T for 45 min at room temperature produced almost uniform hexagonal crystals. We hope to use this technique for other crystal preparation both organic and inorganic for various applications.

Acknowledgements

National Environmental Research Council support for this study by a grant is gratefully acknowledged. The support from Mr. B. Liley, Electron Microscopy and XRD centre, University of Herefordshire, Hatfield is highly appreciated.

References

- [1] K.D. Ghuge, R.R. Angadi, *Indian J. Technol.* 25 (1987) 187.
- [2] T.T. Harkins, *Science* 263 (1994) 958.
- [3] M. Blank, in: *Electromagnetic fields and biological interactions and mechanisms*, Vol. 250, *Advances in Chemistry*, American Chemical Society, Washington DC, 1995, pp. 395–420.
- [4] J.M. Barnthy, *Nature* 200 (1963) 85.
- [5] J.M. Freyssinet, *Biochimie* 66 (1981) 81.
- [6] M.M. Mitrovic, *J. Crystal Growth* 112 (1991) 171.
- [7] M. Mitrovic, *Appl. Phys. A* 51 (1990) 374.
- [8] K. Ohgaki, Y. Makihara, H. Sangawa, *Chem. Eng. Sci.* 49 (1994) 149, 911–913.
- [9] G.E. Evans, *J. Chem. Soc. Faraday Trans. 1* (81)(1985) 673.
- [10] M. Ohring, *The Material Science of Thin films*, Academic Press, New York, pp. 115, 123, 125, 126.
- [11] M.M. Mitrovic, *J. Crystal Growth* 87 (1988) A-39.
- [12] H.E. Lundager Madsen, *J. Crystal Growth* 152 (1995) 94.