

INORGANIC SYNTHESIS
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Preparation of High-Purity Silicon Tetrafluoride
by Thermal Dissociation of Na_2SiF_6

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Abstract—The possibility of preparing high-purity silicon tetrafluoride by the thermal dissociation of pure grade Na_2SiF_6 was studied. The impurity composition of the product was studied by IR and atomic emission spectroscopy and by mass spectrometry.

High-purity silicon tetrafluoride SiF_4 is used for preparing fluorine-doped amorphous hydrogenated silicon [1] and ion implantation of silicon and fluorine into gallium arsenide [2]. Because SiF_4 has no intrinsic absorption bands, it is also used as doping additive to decrease the refractive index of quartz glass, which is very important in manufacture of quartz fibers [3]. Also, silicon tetrafluoride is a convenient compound for centrifugal separation of silicon isotopes [4].

The methods for preparing SiF_4 can be subdivided into four groups.

(1) Reaction of elemental silicon with fluorinating agents F^- , SF_6 , UF_6 , NF_3 [5–10], which is a complex procedure requiring sophisticated equipment.

(2) Fluorination of silicon dioxide [11–15]. This, however, involves problems with hydrolysis of SiF_4 by the reaction by-product, H_2O .

(3) Fluorination of silicon tetrachloride [16–22]. With SiCl_4 as the initial compound, it is necessary to treat SiF_4 to remove impurities of mixed fluorochlorosilanes.

(4) Preparation of SiF_4 from hexafluorosilicic acid H_2SiF_6 and hexafluorosilicates of alkali (Li, K, Na) and alkaline-earth (Ba, Ca) metals [23, 24]. It is possible to decompose H_2SiF_6 [25–27] or metal hexafluorosilicates [28–30] with concentrated acids (H_2SO_4 or H_3PO_4). However, silicon tetrafluoride obtained by acid treatment has low purity.

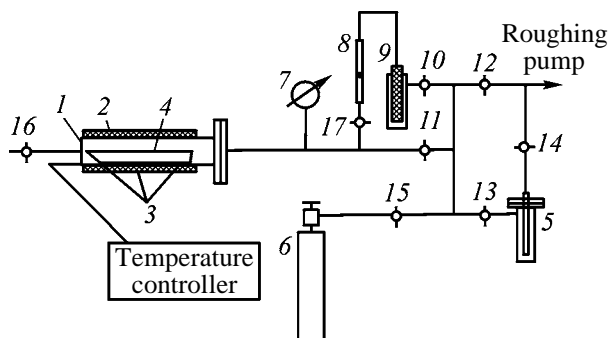
Thermal dissociation of metal hexafluorosilicates is the preferential method [31, 32]. The method is economical and environmentally safe. It was found [33] that SiF_4 obtained by this method from Na_2SiF_6 is relatively pure, because solid sodium fluoride sorbs impurities. The content of the impurities in Na_2SiF_6

and SiF_4 obtained from it is presented in the table [34]. The relative intensity of ions in the mass spectrum of SiF_4 is as follows [34]: SiF_3^+ 96.9, Si_2OF_6^+ 3.04, and SO_2F_3^+ 0.076.

The dissociation pressure of Na_2SiF_6 within 298–968 K has been determined in [35]. A study [36] of the effect exerted by CO_2 , SiO_2 , ZrO_2 , and HfO_2 on the Na_2SiF_6 thermal dissociation showed that addition of SiO_2 considerably decreases the dissociation rate. The thermal dissociation of K_2SiF_6 in the liquid phase (K_2SiF_6 –KCl eutectic) is slower than in the solid

Results of plasma-assisted emission spectroscopic analysis

Element	Content $c \times 10^4$, wt %	
	in Na_2SiF_6	in SiF_4
Li	0.2	0.01
Na	–	1.8
K	8.0	0.3
Mg	6.4	2.3
Ca	18	1.6
B	0.8	<0.01
Al	1.3	1.2
P	5.0	0.08
As	0.2	0.28
V	0.3	<0.01
Cr	8.8	<0.01
Mn	0.4	0.16
Fe	38	0.04
Co	0.7	<0.01
Ni	4.2	<0.01
Cu	0.6	<0.01
Zn	1.0	<0.01
Pb	5.0	0.03
Mo	1.0	<0.01



Setup for the silicon tetrafluoride synthesis. For comments, see text.

phase [37]. The influence of the H_2O partial pressure on the K_2SiF_6 thermal dissociation was studied in [38]. It was found that the SiF_4 being formed reacts with H_2O even at a low partial pressure of water vapor to form various gaseous and X-ray amorphous solid fluorosiloxanes.

EXPERIMENTAL

In this study, SiF_4 was prepared by thermal dissociation of pure grade sodium hexafluorosilicate Na_2SiF_6 . In this case, the yield of SiF_4 approaches 100%, whereas in the case of the K_2SiF_6 thermal dissociation it is considerably lower owing to K_3SiF_7 formation [39]. Moreover, NaF formed in this reaction can be used for sorption purification of SiH_4 to remove SiF_4 impurity in the course of preparation of silane from silicon tetrafluoride.

The impurity content in pure grade Na_2SiF_6 , as determined by laser mass spectrometry, is presented below:

Impurity element	Content, at. %	Impurity element	Content, at. %
B	1×10^{-1}	Cl	1×10^{-3}
C	3×10^{-2}	S	2×10^{-3}
Mg	4×10^{-3}	Ca	3×10^{-2}
Al	4×10^{-4}	Cr	5×10^{-5}
P	2×10^{-2}	Fe	2×10^{-3}

The content of Sc, Ti, V, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, and Bi impurity ions and lanthanides is below the detection limit of this method (1×10^{-4} – 2×10^{-5} at. %).

A setup for the silicon tetrafluoride synthesis is shown schematically in the figure. The synthesis was performed in a stainless steel reactor 1 equipped with a resistance heater 2. The temperature of the heater

was adjusted to within $\pm 0.5^\circ\text{C}$ with an R-133 precision temperature controller and a U-013 power amplifier and measured with a Chromel–Alumel thermocouple 3. A stainless steel boat 4 charged with about 3-kg portion of Na_2SiF_6 was placed into the reactor. The salt was preliminarily dried at 250°C in a vacuum or in a nitrogen flow. Moisture and gases released during preliminary evacuation of Na_2SiF_6 were condensed in a trap 5 cooled with liquid nitrogen.

The thermal dissociation of the salt was performed at 500 – 620°C in a vacuum. Since the Na_2SiF_6 thermal dissociation is a reversible reaction and the degree of dissociation is pressure-dependent, the forming SiF_4 was fed continuously into a 4-l metallic cylinder 6 cooled with liquid nitrogen.

The pressure in the reactor and the rate of the SiF_4 flow from the reactor into the receiving cylinder were monitored with vacuum gage 7 and rotameter 8, respectively. To remove suspended particles, SiF_4 was allowed to pass through a Petryanov cloth filter 9; 10–17 are stopcocks. The SiF_4 yield in the process approached 100%. Up to 1.5 kg of SiF_4 can be obtained on this installation in one process cycle.

The SiF_4 thus obtained was analyzed for the content of molecular impurities by mass spectrometry and IR spectroscopy [40]. Both methods revealed hexafluorodisiloxane as the major impurity. Its content in SiF_4 amounts to several percents, which agrees with the data of [34]. The mass spectrum contained no lines assignable to the BF_3 impurity. The content of metallic impurities in the silicon tetrafluoride obtained, which were concentrated by distilling off the matrix and then analyzed by atomic emission spectroscopy, is presented below:

Impurity	Content, wt %	Impurity	Content, wt %
Al	1×10^{-8}	Mn	3×10^{-10}
Ni	$< 2 \times 10^{-8}$	Ca	7×10^{-8}
Co	$< 7 \times 10^{-8}$	Pb	$< 2 \times 10^{-8}$
Ag	$< 3 \times 10^{-10}$	Sn	$< 2 \times 10^{-8}$
Cd	$< 3 \times 10^{-8}$	Cu	2×10^{-9}
Fe	7×10^{-7}	Ga	$< 4 \times 10^{-9}$
Cr	3×10^{-8}	Sb	$< 1 \times 10^{-7}$
Mg	1×10^{-7}	In	$< 1 \times 10^{-8}$

To perform further isotopic enrichment and use SiF_4 as a doping additive in manufacture of quartz fibers, it was additionally purified by distillation.

CONCLUSION

High-purity SiF_4 was obtained by thermal dissociation of pure grade Na_2SiF_6 . IR spectroscopy and mass

spectrometry revealed hexafluorodisiloxane as the major molecular impurity in SiF₄. According to the data of atomic emission spectroscopy, the SiF₄ prepared contains about 10⁻⁷ wt % metallic impurities.

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REFERENCES

- Nakayama, Y., Wakimura, K., Takahashi, S., *et al.*, *J. Non-Cryst. Solids*, 1985, vols. 77–78, no. 2, pp. 797–800.
- Tamura, A., Inoue, K., and Onuma, T., *Appl. Phys. Lett.*, 1987, vol. 51, no. 9, pp. 1503–1505.
- Kuppers, D., Koenings, J., and Wilson, H., *J. Electrochem. Soc.*, 1978, vol. 125, no. 8, pp. 1298–1302.
- Kvaratskheli, Yu.K., and Sviderskii, M.F., *Konv. Mashinostr.*, 1999, nos. 3–4, pp. 44–48.
- Nikolaev, N.S., Suvorova, S.N., Gurovich, E.I., *et al.*, *Analiticheskaya khimiya flora* (Analytical Chemistry of Fluorine), Moscow: Nauka, 1970.
- Bousguet, J., Carre, J., Claudy, P., *et al.*, *J. Chim. Phys. Phys.-Chim. Biol.*, 1972, vol. 69, no. 6, pp. 1065–1068.
- Johnson, G.K., *J. Chem. Thermodyn.*, 1986, vol. 18, no. 8, pp. 801–802.
- Rai-Choudhury, P., *J. Electrochem. Soc.*, 1971, vol. 118, no. 2, pp. 266–269.
- FRG Patent 3841218.
- Perrin, J., Meot, J., Siefert, J.-M., *et al.*, *Plasma Chem. Plasma Proc.*, 1990, vol. 10, no. 4, pp. 571–587.
- Lieser, K.H., and Rosenbaum, I., *Z. Anorg. Allg. Chem.*, 1967, vol. 351, nos. 5–6, pp. 306–308.
- Green, P.J., and Gard, G.L., *Inorg. Chem.*, 1977, vol. 16, no. 5, pp. 1243–1245.
- JPN Patent 61-247625.
- FRG Patent 3841210.
- US Patent 4382071.
- Boehm, P.H., *Z. Anorg. Allg. Chem.*, 1969, vol. 365, nos. 3–4, pp. 176–179.
- Padma, D.K., and Vasudeva Murthy, A.R., *J. Fluorine Chem.*, 1974, vol. 4, no. 2, pp. 241–242.
- Padma, D.K., Suresh, B.S., and Vasudeva Murthy, A.R., *J. Fluorine Chem.*, 1979, vol. 14, no. 4, pp. 327–329.
- Legasov, V.A. and Marinin, A.S., *Zh. Neorg. Khim.*, 1972, vol. 17, no. 9, pp. 2408–2410.
- Ponomarenko, V.A. and Ignatenko, M.A., *Khimiya ftorkremnievykh soedinenii* (Chemistry of Silicone Fluoride Compounds), Moscow: Nauka, 1979.
- Rakov, E.G., Musorin, V.A., Mel'nichenko, E.I., *et al.*, Abstracts of Papers, *Vsesoyuznaya konferentsiya "Khimiya i tekhnologiya redkikh tsvetnykh metallov i solei"* (All-Union Conf. "Chemistry and Technology of Rare Non-Ferrous Metals and Their Salts"), Frunze, 1986, p. 153.
- Ruff, O., and Albert, K., *Ber.*, 1905, vol. 38, p. 53.
- FRG Patent 3228177.
- GDR Patent 89581.
- Borisov, V.M., and Mel'nikova, S.V., *Zh. Prikl. Khim.*, 1984, vol. 57, no. 3, pp. 705–707.
- Arkhipova, L.N., Tsybina, M.N., Dvoryazhkina, A.N., *et al.*, *Puti ispol'zovaniya kremneftoristykh produktov proizvodstva mineral'nykh udobrenii* (Ways of Utilization of Silicon Fluoride Products from Manufacture of Mineral Fertilizers), Available from ONIITEKHIM, Moscow, November 13, 1985, no. 1101khn.
- US Patent 4470959.
- Zaitsev, V.A., Arkhipova, L.N., Novikov, A.A., *et al.*, *Khim. Prom-st.*, 1974, no. 10, pp. 768–771.
- Lobas, A.P., and Pishchulin, V.P., Abstracts of Papers, *7-i Vsesoyuznyi simpozium po khimii neorganicheskikh ftoridov* (7th All-Union Symp. on the Chemistry of Inorganic Fluorides), Dushanbe, October 9–11, 1984, p. 210.
- Pishchulin, V.P., Kretov, A.V., and Ryzhov, I.E., Abstracts of Papers, *8-i Vsesoyuznyi simpozium po khimii neorganicheskikh ftoridov* (8th All-Union Symp. on the Chemistry of Inorganic Fluorides), Polevskoi, August 25–27, 1987, p. 313.
- FRG Patent 3432678.
- FRG Patent 3217074.
- US Patent 4446120.
- Sanjurjo, A., Nanis, L., Sancier, K., *et al.*, *J. Electrochem. Soc.*, 1981, vol. 128, no. 1, pp. 179–184.
- Chiotti, P., *J. Less-Common Met.*, 1981, vol. 80, no. 1, pp. 97–104.
- Chernov, R.V., and Kovzun, I.G., *Ukr. Khim. Zh.*, 1972, vol. 38, no. 4, pp. 318–323.
- Chernov, R.V. and Dyubova, L.D., Abstracts of Papers, *7-i Vsesoyuznyi simpozium po khimii neorganicheskikh ftoridov* (7th All-Union Symp. on the Chemistry of Inorganic Fluorides), Dushanbe, October 9–11, 1984, p. 343.
- Stodolski, R., and Kolditz, L., *Z. Chem.*, 1985, vol. 25, no. 5, pp. 190–191.
- Kolditz, L., Wilde, W., and Bentrup, U., *Z. Chem.*, 1983, vol. 23, no. 7, pp. 246–247.
- Bulanov, A.D., Balabanov, V.V., Pryakhin, D.A., and Troshin, O.Yu., *Izv. Ross. Akad. Nauk, Neorg. Mater.*, 2002, vol. 38, no. 3, pp. 356–361.