# Reactivity of SiCl and SiF groups in SiO$_2$ glass with mobile interstitial O$_2$ and H$_2$O molecules

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## Abstract

Reactions of common network-bound halogens in synthetic SiO$_2$ glass, SiCl and SiF groups, with interstitial O$_2$ and H$_2$O molecules incorporated by thermally annealing were studied. It was found that the chemical properties are distinctly different between SiCl and SiF groups. SiCl groups react with interstitial O$_2$ and H$_2$O to form interstitial Cl$_2$ and HCl, respectively. In contrast, formation of interstitial F$_2$ and HF due to the reaction of SiF groups with interstitial O$_2$ and H$_2$O is not observed. The reactivity of SiCl and SiF groups is in accord with the properties and thermodynamic data of their respective analogous compounds, SiCl$_4$ and SiF$_4$.
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## 1. Introduction

Synthetic SiO$_2$ glass with low metallic impurity content is a unique optical material of excellent transparency from infrared (IR) to vacuum-ultraviolet (VUV, $\lambda \lesssim 190$ nm) spectral region and of good shape workability. In such high-purity SiO$_2$ glass, a considerable part of radiation-induced color centers are created from strained Si–O–Si bonds, that is, chemical bonds destabilized by residual strain in the glass network. The residual strain can be greatly reduced by incorporating functional groups such as SiCl, SiF and SiOH groups, which terminate the SiO$_2$ glass network, reduce the viscosity and enhance the structural relaxation.

Chemical properties of the network-bound functional groups is a subject of intense interest because they are often involved in radiation-induced defect processes along with mobile species incorporated in interstitial structural voids in SiO$_2$ glass. Recently, we found that interstitial O$_2$ and H$_2$O molecules loaded by thermal annealing convert SiCl groups into interstitial Cl$_2$ and HCl molecules, respectively [1]. It is interesting to examine whether similar reactions take place for SiF groups. Fluorine in the form of SiF groups is an important and deliberately-introduced network-bound halogen dopant in synthetic SiO$_2$ glass, since they are hard to radiolyze and exhibit no optical absorption bands within the 'transparency window' of SiO$_2$ glass ranging from IR to VUV.

In this report, we investigate the difference in reactivity between SiCl and SiF groups utilizing the thermal gas loading in SiO$_2$ glass.

## 2. Experimental procedure

Two types of synthetic SiO$_2$ glasses, denoted as 'Cl-doped' (SiCl, $\sim 7 \times 10^{19}$ cm$^{-3}$; SiOH $< 10^{17}$ cm$^{-3}$; Si–Si,

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$\sim 2 \times 10^{17}$ cm$^{-3}$; $6.5 \times 10 \times 1$ mm$^3$) and 'F-doped' (SiF, $\sim 1 \times 10^{21}$ cm$^{-3}$; SiOH $\sim 2 \times 10^{17}$ cm$^{-3}$; $6.5 \times 10 \times 2$ mm$^3$), were used. O$_2$-loaded samples were prepared by thermally annealing the sample for 240 h at 1000 °C in a sealed silica tube (inner diameter, $\sim 12$ mm; thickness, $\sim 1.2$ mm) filled with $\sim 2$ atm O$_2$ at room temperature. H$_2$O-loaded samples were similarly prepared by thermally annealing the sample with liquid H$_2$O and air in a silica tube. The amount of H$_2$O was controlled to make the partial pressure of H$_2$O during the annealing $\sim 7$ atm. The Cl-doped sample was annealed for 480 h at 400 °C. The F-doped sample was treated for 3720 h at lower temperature, 170 °C, to increase the fraction of interstitial H$_2$O with respect to that of SiOH groups by suppressing the hydrolysis of glass network [2–4]. The samples were characterized by visible–ultraviolet (VIS–UV), Fourier-transform (FT) IR and FT-Raman spectrometers (Hitachi U-4000, Perkin Elmer Spectrum One and Nicolet Model 960, respectively).

## 3. Results

The O$_2$ or H$_2$O loading did not change the appearance of the samples including clarity and surface smoothness. Fig. 1 shows emission spectra of the Cl- and F-doped samples before and after the O$_2$ loading at 1000 °C, measured under excitation with Nd:YAG laser light ($\lambda = 1064$ nm, $\sim 1$ W at sample position). Emission observed before the O$_2$ loading was due to the Raman scattering of SiO$_2$ glass. In the F-doped sample, a Raman band of SiF groups located at $\sim 945$ cm$^{-1}$ [5–8] was also seen. The O$_2$ loading caused a new emission band at $\sim 1535$ cm$^{-1}$ (absolute energy, $\sim 7860$ cm$^{-1}$) attributed to the photoluminescence (PL) of interstitial O$_2$ [9]. The concentration of interstitial O$_2$ evaluated from the PL intensity normalized to that of the SiO$_2$ Raman bands [10] were $\sim 2 \times 10^{17}$ and $\sim 3 \times 10^{17}$ cm$^{-3}$ for the Cl- and F-doped samples, respectively.

Fig. 2 shows UV–VIS absorption spectra of Cl- and F-doped samples before and after the O$_2$ loading. In the Cl-
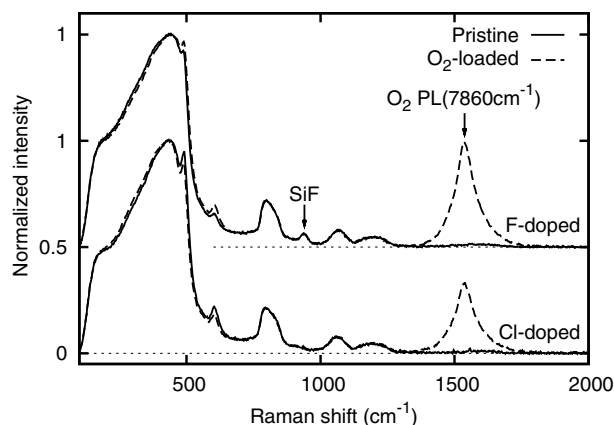
doped sample, an absorption band located at 3.8 eV [11], which is assigned to interstitial Cl$_2$ [12–14], was formed by the O$_2$ loading [1]. In contrast, the O$_2$ loading did not induce any obvious absorption bands in the F-doped sample between 2 and 6 eV. The evaluated concentration of interstitial Cl$_2$ was $\sim 2 \times 10^{18}$ cm$^{-3}$ ($\sim 5\%$ of total Cl atoms) and the detection limit of interstitial F$_2$ was $\sim 5 \times 10^{17}$ cm$^{-3}$ ($<0.1\%$ of total F atoms), assuming that the absorption cross sections are identical to those of gaseous Cl$_2$ [15] and F$_2$ [16], respectively.

Fig. 3 shows IR absorption spectra of Cl- and F-doped samples before and after the H$_2$O loading. The H$_2$O loading incorporated $\sim 10^{19}$–$10^{20}$ cm$^{-3}$ SiOH groups and $\sim 10^{18}$–$10^{19}$ cm$^{-3}$ interstitial H$_2$O [17], whose absorption bands are located at $\sim 3670$ and $\sim 3300$–$3500$ cm$^{-1}$, respectively [3,4]. No other distinct induced absorption was found in the F-doped sample. In contrast, an absorption band located at $\sim 2815$ cm$^{-1}$ [3,11,18,19], which is due to interstitial HCl [1], was observed in the Cl-doped sample. The concentration of HCl was calculated to be $\sim 1 \times 10^{19}$ cm$^{-3}$ ($\sim 15\%$ of total Cl atoms) using a peak absorption cross section ($\sim 2 \times 10^{-19}$ cm$^2$ [1]), which was
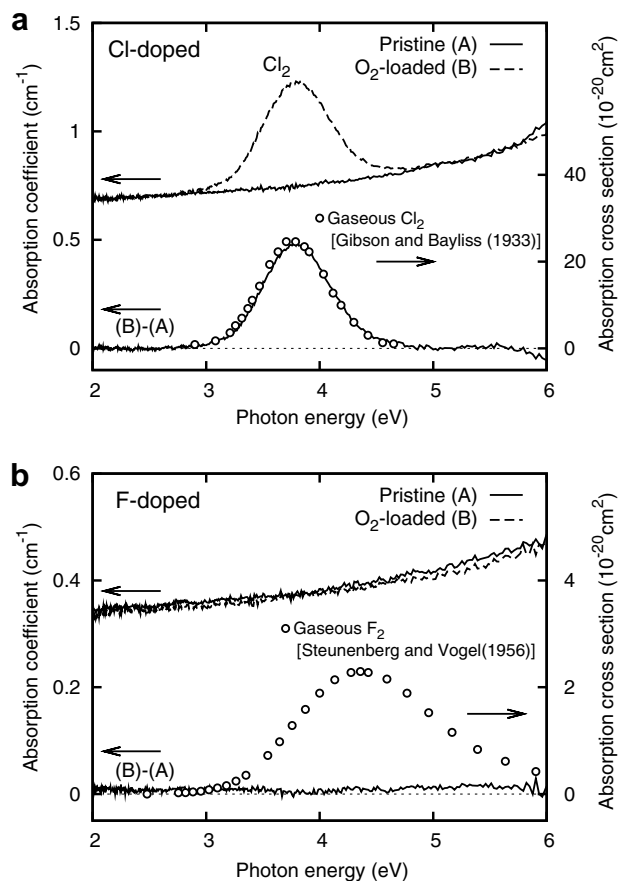
Fig. 2. VIS–UV absorption spectra of Cl- and F-doped SiO$_2$ glasses before and after O$_2$ loading (1000 °C, 240 h), and their difference spectra. Optical loss in the pristine samples is due to the surface reflection. Absorption cross section spectra of gaseous Cl$_2$ and F$_2$ molecules are taken from Refs. [15,16].

Fig. 1. IR emission spectra of Cl- and F-doped SiO$_2$ glasses under excitation with Nd:YAG laser light ($\lambda = 1064$ nm) before and after O$_2$ loading (1000 °C, 240 h). The emission consists of Raman bands of SiO$_2$ glass ($<1400$ cm$^{-1}$) and an O$_2$ photoluminescence band ($\sim 1535$ cm$^{-1}$, absolute energy $\sim 7860$ cm$^{-1}$) [9,10].
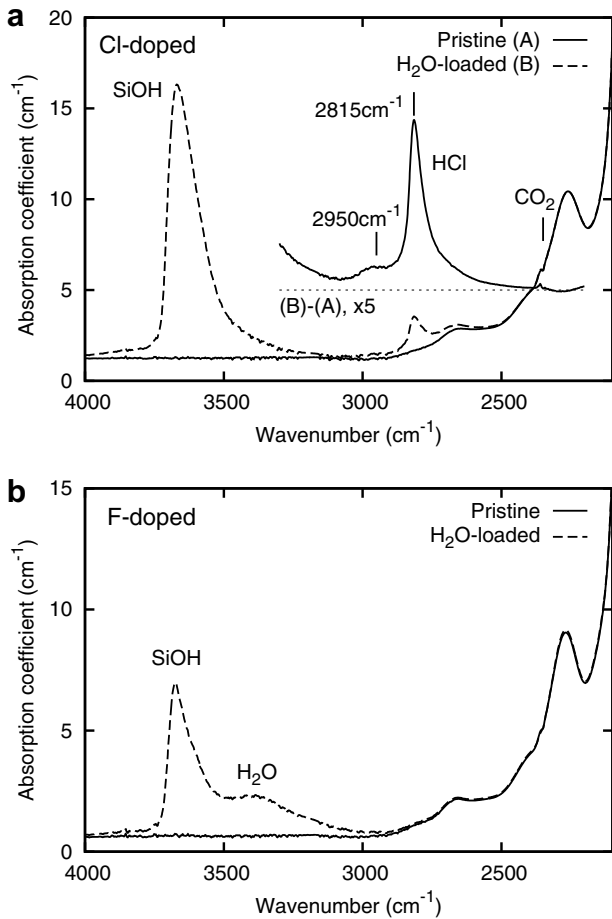
Fig. 3. IR absorption spectra of Cl- and F-doped $SiO_2$ glasses before and after $H_2O$ loading (400 °C, 480 h for Cl-doped sample; 170 °C, 3720 h for F-doped sample).

Table 1
Standard Gibbs energy change of reactions $\Delta G°$ at 298 K

| Reactions | $\Delta G°$ (kJ mol Si$^{-1}$)[a] |
|---|---|
| $SiCl_4(g) + O_2(g) \rightarrow SiO_2(s) + 2Cl_2(g)$ | −240 |
| $SiCl_4(g) + 4H_2O(g) \rightarrow Si(OH)_4(s) + 4HCl(g)$ | −180 |
| $SiCl_4(g) + 2H_2O(g) \rightarrow SiO_2(s) + 4HCl(g)$ | −160 |
| $SiF_4(g) + O_2(g) \rightarrow SiO_2(s) + 2F_2(g)$ | 720 |
| $SiF_4(g) + 4H_2O(g) \rightarrow Si(OH)_4(s) + 4HF(g)$ | 50 |
| $SiF_4(g) + 2H_2O(g) \rightarrow SiO_2(s) + 4HF(g)$ | 70 |
| $SiF_4(g) + 2/3H_2O(g) \rightarrow 1/3SiO_2(s) + 2/3H_2SiF_6$ | $-290 \pm 130$[b] |

(s) and (g) denote the solid and gaseous phases, respectively.
[a] Calculated from the standard Gibbs energy of formation at 298 K, reported in Ref. [25].
[b] Estimate value derived assuming that the standard Gibbs energy of formation of $H_2SiF_6$ is $-2600 \pm 200$ kJ mol$^{-1}$ with considering that of $Na_2SiF_6$ ($-2750$ kJ mol$^{-1}$), $K_2SiF_6$ ($-2800$ kJ mol$^{-1}$) and $(NH_4)_2SiF_6$ ($-2370$ kJ mol$^{-1}$).

evaluated assuming that interstitial HCl and HCl dissolved in rare-gas matrices [20,21] have the same absorption intensity.

## 4. Discussion

$O_2$ loading forms interstitial $Cl_2$ in Cl-doped $SiO_2$ glasses (Fig. 2) [1]. From an analogy of this reaction with the oxidation of $SiCl_4$, which is spontaneous due to a large negative change of the Gibbs free energy, $\Delta G°$ (Table 1), the formation of interstitial $Cl_2$ is attributed to the oxidation of SiCl groups [1]:

$$2\equiv SiCl + 1/2O_2 \rightarrow \equiv Si-O-Si\equiv + Cl_2. \quad (1)$$
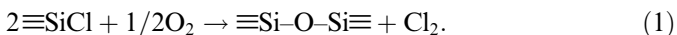
The oxidation of SiCl groups (Eq. (1)) and $SiCl_4$ are of practical importance in preparing 'dry' $SiO_2$ glasses without post-dehydration by the plasma chemical vapor deposition.

$SiF_4$ is very stable against oxidation as expected from a large positive $\Delta G°$ (Table 1). Hence, it is unlikely that SiF groups, a derivative of $SiF_4$, react with interstitial $O_2$ as
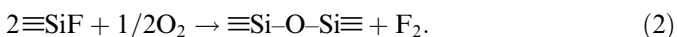
$$2\equiv SiF + 1/2O_2 \rightarrow \equiv Si-O-Si\equiv + F_2. \quad (2)$$

Indeed, interstitial $F_2$ is not detected in the F-doped $SiO_2$ glass loaded with $O_2$ (Fig. 2).

$SiCl_4$ reacts spontaneously with $H_2O$ (Table 1). Actually, hydrolysis and polycondensation of $SiCl_4$ in oxyhydrogen flame or aqueous solutions are widely used to fabricate $SiO_2$. Thus, it is probable that interstitial HCl is generated by analogous reactions:

$$\equiv SiCl + H_2O \rightarrow \equiv SiOH + HCl, \quad (3)$$

$$2\equiv SiCl + H_2O \rightarrow \equiv Si-O-Si\equiv + 2HCl. \quad (4)$$
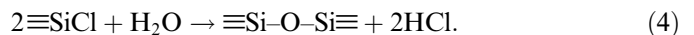
Formation of interstitial HCl is confirmed by its characteristic IR absorption band at 2815 cm$^{-1}$ (Fig. 3) [1], which is slightly shifted to lower energy side compared with that of a free HCl molecule at 2886 cm$^{-1}$ [22]. This shift is likely due to the hydrogen bonding and dispersion interaction, induced by the surrounding $H_2O$ molecules, SiOH groups and oxygen atoms in the $SiO_2$ network.

$SiF_4$ promptly reacts with $H_2O$ to produce $SiO_2$ and $H_2SiF_6$ (Table 1). This reaction can be separately written as

$$SiF_4 + 2H_2O \rightarrow SiO_2 + 4HF, \quad (5)$$

$$SiF_4 + 2HF \rightarrow H_2SiF_6. \quad (6)$$
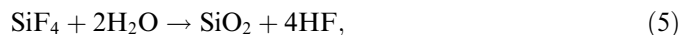
In fact, the disproportionation of $SiF_4$ is aided by a large affinity between $SiF_4$ and HF (Eq. (6)): a part of $SiF_4$ acts as an HF trap and thereby proceeds the hydrolysis of $SiF_4$ (Eq. (5)), which itself is energetically unfavorable (Table 1).

As shown by the detection of interstitial HCl, IR absorption may also be used to check the possible formation of interstitial HF by reactions

$$\equiv SiF + H_2O \rightarrow \equiv SiOH + HF, \quad (7)$$

$$2\equiv SiF + H_2O \rightarrow \equiv Si-O-Si\equiv + 2HF. \quad (8)$$
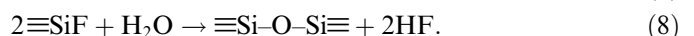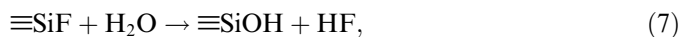
A free HF molecule has an absorption band at 3962 cm$^{-1}$ [22] but this band can be shifted to lower energy side for HF in condensed media. For example, peak position of HF molecules dissolved in rare-gas solids is widely varied between ~4000 and 3000 cm$^{-1}$ by clustering [23] and by hydrogen bonding with codoped $H_2O$ molecules [24]. Unfortunately, this spectral range significantly overlaps

with the absorption bands of SiOH groups and interstitial $H_2O$, making the search for the HF band difficult. Nevertheless, an IR absorption band of intensity comparable to the interstitial HCl band (Fig. 3, top) should have been detectable if it were present. On the other hand, its absence (Fig. 3, bottom) is consistent with the expectations from the thermodynamic data listed in Table 1. Thus, it is considered that interstitial HF is not formed by $H_2O$ loading in F-doped $SiO_2$ glasses.

## 5. Conclusions

Reactivity of SiCl and SiF groups was investigated by incorporating $O_2$ and $H_2O$ molecules from ambient atmosphere by thermal annealing. SiCl groups were decomposed by $O_2$ and $H_2O$ into interstitial $Cl_2$ and HCl, respectively. However, it seems likely that SiF groups do not undergo similar reactions to generate interstitial $F_2$ and HF. It is possible to predict the reactivity of SiCl and SiF groups from the Gibbs free energy change of reactions of the corresponding tetrahalogenosilanes, $SiF_4$ and $SiCl_4$. It is shown that SiF groups are much more chemically inert than SiCl groups, confirming the utility of SiF groups as dopants to relax the glass structure and to suppress photochemical reactions in $SiO_2$ glass.

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