# Interaction between SiO$_2$ and a KF–KCl–K$_2$SiF$_6$ Melt

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ABSTRACT: The solubility mechanism of silica in a fluoride–chloride melt has been determined in situ using Raman spectroscopy. The spectroscopy data revealed that the silica solubility process involved Si–O bond breakage and Si–F bond formation. The process results in the formation of silicate complexes, fluorine-bearing silicate complexes, and silicon tetrafluoride in the melt. Mass spectrometry of the vapor phase over the KF–KCl–K$_2$SiF$_6$ and KF–KCl–K$_2$SiF$_6$–SiO$_2$ melts and differential scanning calorimetry coupled with thermal gravimetric analysis of these melts were performed to verify the silica solubility mechanism.
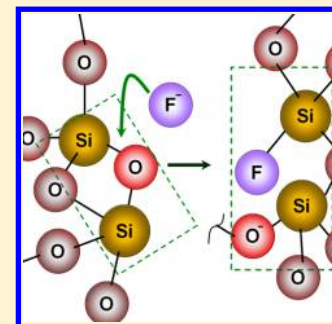
INTRODUCTION

Silica solubility in fluoride–chloride melts was under investigation in our previous work.[1] It was found to be greatly dependent on melt composition. This fact can be explained by the difference in the interaction mechanisms attributed to separate components of the salt mixture. The final result of silica dissolution in a molten halide mixture is a halide–oxide melt which presents substances of different natures. Molten salts are ionic liquids but silica is a molecular compound with bridging bonds. In the case of low silica solubility in molten salts, it is necessary to find the composition that affords maximal solubility.

Several studies have been devoted to the interaction of SiO$_2$ with fluoride systems at high temperatures. Anfilogov et al. studied molten silicate glasses using Raman spectroscopy and found that dissolution of a chlorine anion in SiO$_2$ did not cause Si–O–Si bond breakage, whereas dissolution of a fluoride anion did cause bond breakage.[2] Cleavage of the Si–O bond is possible if the SiO$_2$ concentration in the MF–SiO$_2$ (where M is alkali metal) mixture is 95 mol % and higher. The classification of the structural units presented in these molten silicate glasses was provided. Mysen et al. studied the interaction mechanisms in the SiO$_2$–NaF and SiO$_2$–AlF$_3$ systems using Raman spectroscopy, and the stable structural units $[SiO_4]^{4-}$, $[Si_2O_5]^{2-}$ and $[SiO_3F]^{3-}$, $[Si_4O_7F_2]$ were established.[3]

K$_2$SiF$_6$ and oxyfluoride–silicate complex anions of the $[SiO_2F_2]^{2-}$ type were formed due to silicon dioxide dissolution in melts based on XRD analysis of alkali fluorides.[4,5] K$_2$O can also be formed at very high KF concentrations. XRD analysis[6] demonstrates that the interaction between KF and SiO$_2$ can proceed with K$_3$SiF$_7$ formation. The interaction between KF and SiO$_2$ is accompanied by the formation of the 4KF·SiO$_2$ type silicates.[7]

However, there are no available data on the interaction between SiO$_2$ and halide melts because of the difficulties encountered in the high temperature experiment: high corrosion activity of fluoride salts and limited choice of inert materials. The objective of this study is to obtain data on the structure of basic melt KF–KCl–K$_2$SiF$_6$ and its change during silica dissolution using Raman spectroscopy.

Raman spectroscopy allows detection of the melt complex structure in situ. The method provides sufficient data to determine the composition of ionic complexes and the compositional changes due to SiO$_2$ dissolution in the KF–KCl–K$_2$SiF$_6$ melts.

To verify the Raman spectroscopy results, the changes in the salt phase composition were studied using differential scanning calorimetry (DSC) with analysis of the vapor phase over the melt by mass spectrometry. The RFA analysis was also used to check the interaction products in samples under investigation.

EXPERIMENTAL SECTION

Chemicals. The electrolytes were prepared from chemically pure grade KF·HF and KCl and analytically pure grade K$_2$SiF$_6$. Potassium chloride was obtained from Uralkalii, and KH·HF and hexafluorosilicate was obtained from Vekton.

Fine powder silica was supplied by Russian Magnesium Company. It was preliminarily dried in a quartz crucible for 3 h under air atmosphere at 773 K. Before the experiment, potassium chloride and potassium hexafluorosilicate were specially prepared.[1]

A mixture of KCl and KF·HF was heated in a glassy carbon crucible to 973 K and was maintained at this temperature for 4–5 h. The HF was removed via the thermal decomposition of KF·HF. Then the needed amounts of the K$_2$SiF$_6$ and SiO$_2$ were added. The melt was kept at constant stirring for 30 min and

then was transferred to a graphite crucible. The prepared melts were kept in a drybox.

The concentration of the admixtures was measured by mass spectrometry. The admixture content did not exceed 0.001 wt %. The XRD analysis of the silicon powders was performed using a Rigaku DMAX-2200/pc microscope.

Raman Spectroscopy. The Raman spectroscopy setup is presented in Figure 1. The nickel tube (7) with the salt mixture
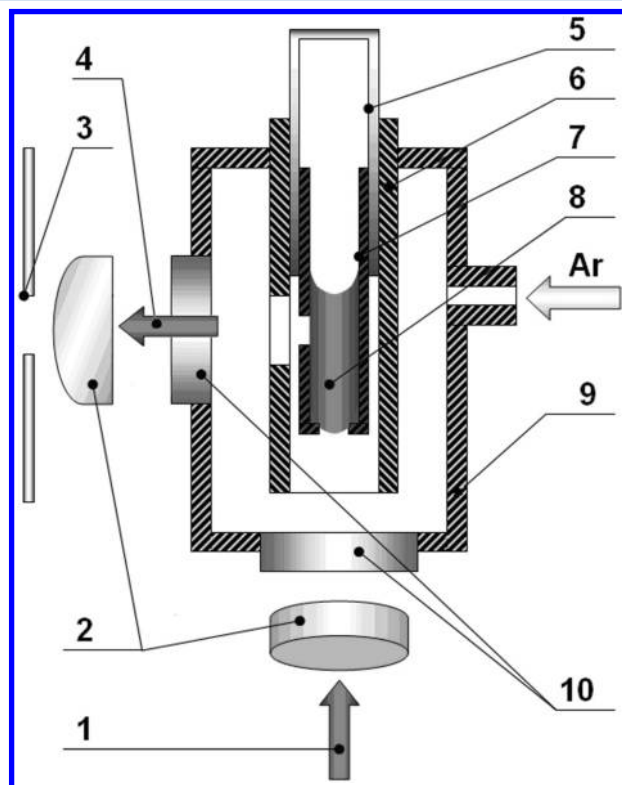

Figure 1. The Raman spectra recording setup: 1, laser beam; 2, focus object-glass; 3, monochromatic entrance slit; 4, direction of the scattering light; 5, quartz holder; 6, electric furnace; 7, optic nickel cell; 8, the melt under study; 9, block; 10, optic quartz windows.

(8) was placed in the optic cell. The optic cell contained a side port for scattered light penetration. The cell was placed in a quartz holder (5) and inserted into a block of a previously heated furnace. The measurements were performed under argon atmosphere.

The melt was maintained by surface tension forces. The height of the melt in the cell was approximately 10 mm. The laser beam passed through the focus object-glass (2) and the optic quartz window (10). The object-glass at the spectrometer entrance slit focused the scattering emission in the melt.

Raman spectra were obtained by the DFS-24 double spectrometer in scanning mode (the optic width of the slit was 15 cm^{-1}, and the scanning rate was 1.1 nm·min^{-1}). The DPSS laser served as the emission source (λ = 532 nm, 300 mW).

Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG) of the Salt Samples and Mass Spectroscopy Analysis of the Vapor Phase. Changes in the vapor-phase composition were studied using a QMS 403 Aëlos mass spectrometer along with a synchronous thermal analysis set consisting of differential scanning calorimetry (DSC) and thermogravimetry (TG) on an STA 449C Jupiter

thermal analyzer (Netsch, Germany). The QMS 403C mass spectrometer and the thermal analyzer were connected by a heated quartz capillary.

The prepared samples were placed into the platinum crucibles with pierced lids. Changes in the sample mass and in the heat flow (DSC signal) were recorded while heating. All of the measurements were performed under Ar atmosphere, and the heating rate was 10 deg·min^{-1}.

The melt vapors in the inert gas flow were transferred to the mass spectrometer camera via the capillary. Raman experiments were conducted with samples of different compositions compared to TG, DSC, and MS experiments because of different sensitivities of the methods applied. The DSC method is more sensitive than Raman spectroscopy; thus, the silica content in Raman spectroscopy experiments was higher. The compositions for TG, DSC, and MS experiments were measured at lower liquidus temperatures to provide sufficient vapor pressure above the melt and to obtain reliable data on gas-phase composition.

■ RESULTS AND DISCUSSION

Figure 2 illustrates the Raman spectra for the KF (25 mol %)−KCl (65 mol %)−K$_2$SiF$_6$ (10 mol %) melt. Wide vibrational
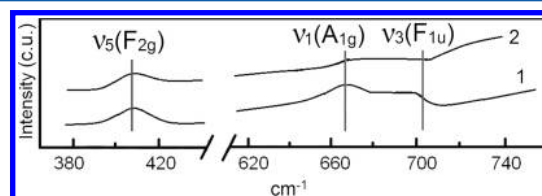

Figure 2. Raman spectra of the KF−KCl−K$_2$SiF$_6$ melt at temperatures: 1, 988 K; 2, 1043 K.

bands of low intensity with maxima at 409, 668, and 703 cm^{-1} were registered in the low-frequency spectral region. These bands are related to the following vibration types of the SiF$_6^{2-}$ ion: ν_5 (F$_{2g}$) is a valence symmetric type, ν_1 (A$_{1g}$) is a valence symmetric type, and ν_3 (F$_{1u}$) is a valence asymmetric type.[8] KF and KCl in both the solid and molten states in the low frequency region have a shoulder on the Rayleigh scattering wing and have no separate vibrational bands in the high frequency region. As the temperature increased, the intensity of the vibrational bands decreased (Figure 2, spectrum 2) due to thermal dissociation of the SiF$_6^{2-}$ ion.[9]

The spectra for the KF (65 mol %)−KCl (25 mol %)−K$_2$SiF$_6$ (10 mol %) melt with 5 mol % SiO$_2$ at 1043 K were taken at the following melt exposition times: 10, 40, 100, and 130 min (Figure 3). To interpret the high frequency region of the vibrational spectra, a previously determined classification of silicate structural units was used.[2] The definitions of the structural units for the corresponding vibrational frequencies are given in Figure 3. Silicate structural units are presented as [SiO$_A$]$^{B-}$ where A is the number of oxygen ions in the silicate group, and B is the number of nonbridging bonds in the silicate complex.

The vibrational bands in the Raman spectra were correlated as follows (Figure 3): the band with the maximum at 1100−1200 cm^{-1} corresponds to the valence nonsymmetric vibrations of bonds in tetrahedrons [SiO$_4$]^0 (Q$_4$ structural unit) with all four bridging oxygen atoms. The band with the maximum at 1050−1100 cm^{-1} is related to the valence nonsymmetric vibrations of unbridged bonds in [SiO$_4$]$^{1-}$ tetrahedrons with
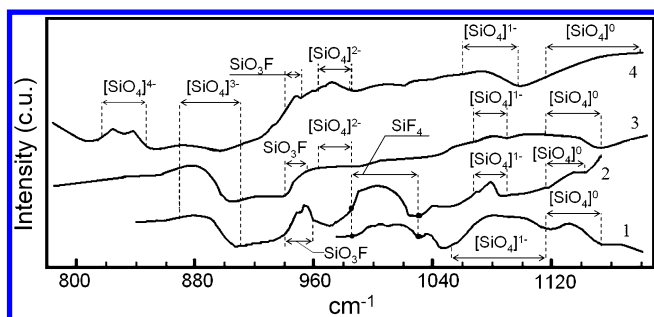
Figure 3. Changes in the Raman spectra of the KF−KCl−K$_2$SiF$_6$−SiO$_2$ melt at $T = 1043$ K with time: 1, 10 min; 2, 40 min; 3, 100 min; 4, 130 min.

one nonbridging oxygen atom (Q$_3$ structural unit). The bands with the maxima at 950−980 cm^{-1} and 900 cm^{-1} correspond to the vibrations of the end group in the [SiO$_4$]$^{2-}$ and [SiO$_4$]$^{3-}$ tetrahedrons with two or three nonbridging oxygen atoms (Q$_2$ and Q$_1$ structural unit). The band with the maximum near 850 cm^{-1} is due to the valence nonsymmetric vibration of isolated [SiO$_4$]$^{4-}$ tetrahedrons with all nonbridging oxygen atoms (Q$_0$ structural unit).

Analysis of the Raman spectra shows that an increase in the exposition time results in dissolution (depolymerization) of the three-dimensional SiO$_2$ lattice (the 1140 cm^{-1} band related to the asymmetric vibrations of the Q$_4$ structure disappears) and a change in the type of silicate structural units from Q$_4$ to Q$_0$. Breaking of the Si−O−Si bonds occurred with the formation of one, two, or three (Q$_3$, Q$_2$, or Q$_1$, respectively) structural units of nonbridging oxygen atoms and isolated [SiO$_4$]$^{4-}$ tetrahedrons (Figure 3, spectrum 4).

As the structural units dissolve and divide into smaller units, the tetrahedrons become more distorted (the length of the valence bonds and bond angles change), which results in significant widening of the vibrational bands in the high frequency spectral region, causing their overlap, and thus a single "plateau" instead of individual bands is observed in the spectrum (Figure 3, spectra 3 and 4). There is a vibrational band in the 1000 cm^{-1} region, which may be related to the deformation vibrations ν_3 of the SiF$_4$ molecules formed from the thermal decomposition of potassium hexfluorosilicate.[10]

The vibrational band with the maximum at 940 cm^{-1} (Figure 3, spectra 2−4), which is not present in the silicate Raman spectra,[2] can be related to the Si−F bond in the oxyfluoride tetrahedron [SiO$_3$F]. This vibrational band was observed in the Raman spectra for the SiO$_2$−NaF composition[8] at 935 cm^{-1} and in spectra of silicate glasses doped by fluorines[11] at 945 cm^{-1}. The stability of the [SiO$_3$F]$^{3-}$ tetrahedron was explained by the formation of electroneutral [Si$_4$O$_7$F$_2$] particles in the silicate melt. Each particle includes two tetrahedrons.[3]

The vibrational band responsible for Si−F bonds was observed at all exposition times. The [SiO$_3$F] groups are formed in a noticeable amount in NaF−SiO$_2$ melts[2] until the NaF:SiO$_2$ ratio is equal to 1. In addition, the interaction of silicon dioxide with sodium fluoride in open crucibles is accompanied by SiF$_4$ formation. The formation of other oxyfluoride groups is also possible due to the high KF concentration in the molten mixture under study.[4,5]

Thus, the Si−F bond forms during the SiO$_2$ dissolution in the KF−KCl−K$_2$SiF$_6$ melt as the Si−O−Si bridges in the three-dimensional lattice break. While dissolving, the oxygen ion in the silicate tetrahedron is replaced by a fluoride anion. The

SiO$_2$ dissolution in the KF−KCl−K$_2$SiF$_6$ melt proceeds according to the following scheme: Q$_4$ → Q$_3$ → Q$_2$ → Q$_1$ → Q$_0$. As a result, dissolution of SiO$_2$ leads to the appearance of isolated [SiO$_4$]$^{4-}$ silicate tetrahedrons of the Q$_0$ structure and gaseous SiF$_4$ in the melt through the formation of sufficiently stable oxyfluoride silicon complexes.

To verify the results from the interaction between SiO$_2$ and the KF−KCl−K$_2$SiF$_6$ melt obtained by Raman spectroscopy, mass spectrometry of the gas phase over the melt coupled with the DSC and TG analysis of the samples was performed in the temperature range of 296−1073 K. DSC and TG data for the KF (40.5 mol %)−KCl (49.5 mol %)−K$_2$SiF$_6$ (10 mol %) melt and data on the mass spectrometry of the gas phase are presented in Figure 4.
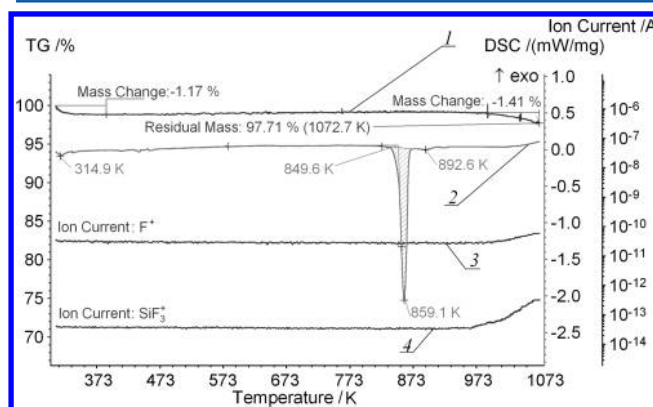

Figure 4. Results of the DSC and TG analysis of the KF (40.5 mol %)−KCl (49.5 mol %)−K$_2$SiF$_6$ (10 mol %) melt and the vapor-phase mass spectrometry.

According to the DSC data (Figure 4, curve 2), the KF (40.5 mol %)−KCl (49.5 mol %)−K$_2$SiF$_6$ (10 mol %) mixture melted at 849.6 K (the melting peak temperature was 859.1 K), and the liquidus temperature was 892.6 K. This result is in good agreement with the literature data.[12]

The sample mass loss at the temperatures up to 373 K (Figure 4, curve 1) is due to the removal of the moisture absorbed at the surface. A noticeable mass loss of the sample (1.4%) was observed in the temperature range of 993−1073 K. The mass spectrometry study of the gas phase (Figure 4, curve 3 and 4) demonstrates that the sample mass loss is due to the increasing concentration of SiF$_4$ in the gas phase.

The data suggest that at the temperatures over 993 K the decomposition of potassium hexflourosilicate with gaseous SiF$_4$ emission proceeds exhaustively in the melts under study.[9] In this case, the composition of the melt changes and it is enriched with KF. The liquidus temperature of this type of salt mixture shifts to the region of higher temperatures because of the formation of a higher melting compound, K$_3$SiF$_7$. To verify the K$_3$SiF$_7$ formation, the KF−KCl−K$_2$SiF$_6$ sample was heated to 1000 K, frozen, and studied using XRD analysis. The K$_3$SiF$_7$ compound was observed in the frozen melt (Figure 5).

The DSC and TG signals changed as 0.9 mol % of SiO$_2$ was added to the KF (40.5 mol %)−KCl (49.5 mol %)−K$_2$SiF$_6$ (10 mol %) melt (Figure 6). At temperatures lower than 373 K, there was a sample mass loss of 1.69% because of absorbed moisture removal (Figure 6, curve 1). Addition of 0.9 mol % of SiO$_2$ leads to an increase in the mass loss due to the increasing SiF$_4$ emission (Figure 6, curve 4), which can be related to the K$_3$SiF$_7$ decomposition. Therefore, SiO$_2$ addition to the KF−
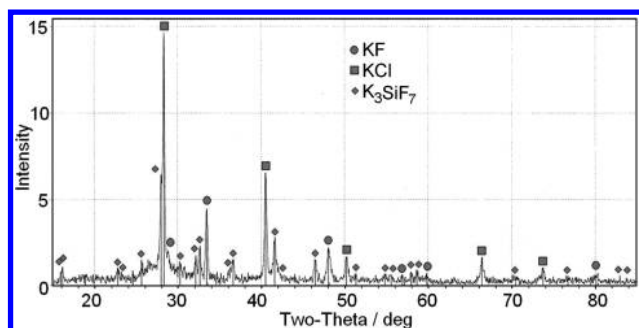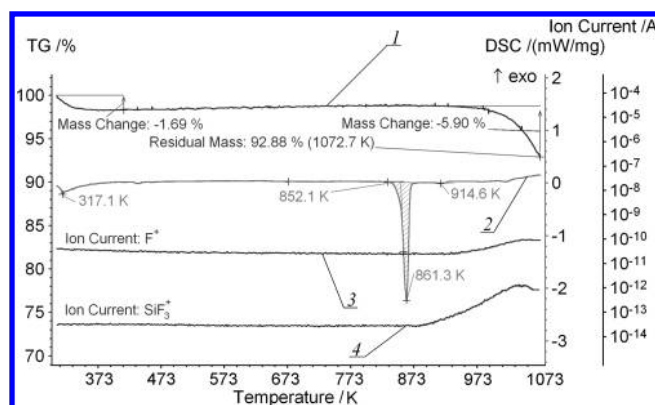
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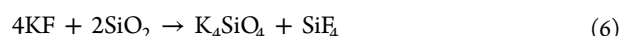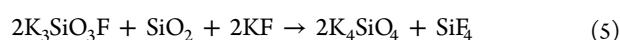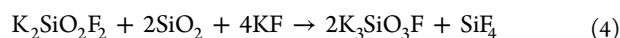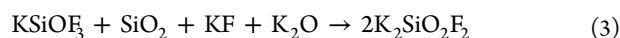**Figure 5.** XRD data for the solid $KF-KCl-K_2SiF_6$ melt.

Figure 6. Results of the DSC, TG analysis, and vapor-phase mass spectrometry of the KF (40.5 mol %)−KCl (49.5 mol %)−K_2SiF_6 (10 mol %) melt with 0.9 mol % of SiO_2.

$KCl-K_2SiF_6$ melt results in increased SiF_4 emission. Thus, the studies on the changes of the gas-phase composition by mass spectrometry verify the data obtained by the Raman spectroscopy method.

Formation of the structural units, including isolated $[SiO_4]^{4-}$ tetrahedrons and silicon oxyfluoride complex anions, was observed because of the interaction between SiO_2 and $KF-KCl-K_2SiF_6$. The TG method determined that addition of 0.9 mol % SiO_2 to the $KF-KCl-K_2SiF_6$ melt results in an additional mass loss of the melt. The melt mass loss is accompanied by increased SiF_4 emission because of K_3SiF_7 decomposition. In accordance with published data,[4,5] silicon oxyfluoride complexes of the $[SiO_2F_2]^{2-}$ and K_2O types may be formed from the interaction between SiO_2 and KF. The SiO_2 dissolution in $KF-K_2SiF_6$ melts is accompanied by K_3SiF_7 formation.[4]

Data obtained in this study and previously published data were used to derive the following reactions for the interaction between SiO_2 and the melt components:

$$3KF + SiO_2 \rightarrow KSiOF_3 + K_2O \tag{1}$$

$$2K_2O + SiO_2 \rightarrow K_4SiO_4 \tag{2}$$

$$KSiOF_3 + SiO_2 + KF + K_2O \rightarrow 2K_2SiO_2F_2 \tag{3}$$

$$K_2SiO_2F_2 + 2SiO_2 + 4KF \rightarrow 2K_3SiO_3F + SiF_4 \tag{4}$$

$$2K_3SiO_3F + SiO_2 + 2KF \rightarrow 2K_4SiO_4 + SiF_4 \tag{5}$$

$$4KF + 2SiO_2 \rightarrow K_4SiO_4 + SiF_4 \tag{6}$$

As SiO_2 is added to the melt in this study, the oxide and alkali metal oxyfluorosilicates are formed (reaction 1). At very high SiO_2 concentrations, potassium silicates and oxyfluorosilicates are formed.

SiF_4 emission under experimental conditions is possible not only via reactions 4−6 but also using the K_3SiF_7 thermal decomposition reaction,[9] according to the following equation:

$$3K_2SiF_6 = 2K_3SiF_7 + SiF_4\uparrow \tag{7}$$

The Raman spectroscopy data also prove that Si has two basic forms in the melt, a silicate form and an oxyfluoride form. The interaction between SiO_2 and the $KF-KCl-K_2SiF_6$ melt is accompanied by reactions 1−6, which lead to changes in the ionic composition of the melt and, hence, to changes in the physical−chemical properties of the salt mixture.

■ CONCLUSIONS

These studies allowed the determination of the SiO_2 dissolution mechanism in $KF-KCl-K_2SiF_6$ melts. SiO_2 dissolution proceeds due to Si−O bond breakage and Si−F bond formation. SiO_2 dissolution in the $KF-KCl-K_2SiF_6$ melt is accompanied by the formation of isolated silicate tetrahedrons, silicon oxyfluoride groups, and gaseous silicon tetrafluoride. SiO_2 dissolution in the melt also results in the formation of two stable forms, the silicate and oxyfluoride ion groups.

The TG method determined that SiO_2 addition to the $KF-KCl-K_2SiF_6$ melt leads to an increased mass loss at temperatures higher than the melting point of the mixture. The mass spectrometry method detected that the mass loss occurred due to SiF_4 formation.

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Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Zaikov, Yu.P.; Redkin, A. A.; Apisarov, A. P.; Korzun, I. V.; Kulik, N. P.; Isakov, A. V.; Kataev, A. A.; Chemezov, O. V. Silica Solubility in Molten Fluoride−Chloride Electrolytes and Density of $KF-KCl-K_2SiF_6-SiO_2$ Melts. *J. Chem. Eng. Data* **2013**, *58* (4), 932−937.
(2) Anfilogov, V. N.; Bykov, V. N.; Osipov, A. A. *Silicate melts*; Nauka: Moscow, Russia, 2005.
(3) Mysen, B. O.; Virgo, D. Interaction between fluorine and silica in quenched melts on the SiO_2-AlF_3 and SiO_2-NaF determined by Raman spectroscopy. *Phys. Chem. Miner.* **1985**, *12*, 77−85.
(4) Chernov, R. V.; Moshnenko, V. M. Study of the silicon dioxide dissolution in the alkali fluoride melts. *Ukr. Chem. J.* **1976**, *42* (11), 1137−1139.
(5) Chernov, R. V.; Dyubova, L. D. Chemical processes at powder-like silicon extraction from silicofluoride melts. *Russ. J. Chem. Technol.* **1989**, *2*, 16−22.
(6) Boyko, O. I. Interaction between silicon dioxide and fluoride-chloride systems. *Ukr. Chem. J.* **1997**, *63* (6), 89−93.
(7) Konakov, V. G.; Pivovarov, M. M. Interaction between components in the $KF-SiO_2$ system. *Glass Phys. Chem.* **2003**, *29* (1), 69−74.
(8) Trefler, M.; Wilkinson, G. Motion of ammonium ions in non-cubic crystal sites. *Discuss. Faraday Soc.* **1969**, *48*, 108−115.
(9) Stodolsky, R.; Kloditz, L. Some aspects of real structure and thermal decomposition of K_2SiF_6. *J. Fluor. Chem.* **1985**, *1* (2), 73.

(10) Bessette, F.; Cabana, A.; Fournier, R.; Savoie, R. Infrared and Raman spectra of liquid and crystal band silicon tetrafluoride. *Can. J. Chem.* **1970**, *48*, 410−416.

(11) Dumas, P.; Corset, J.; Carvalho, W.; Levy, Y.; Neumann, Y. Fluorine doped vitreous silica analysis of fiber optic performs by vibration spectroscopy. *J. Non-Cryst. Solids* **1982**, *47*, 239−242.

(12) Boyko, O. I.; Chernov, R. V. Phase Diagram of the KF−KCl−K_2SiF_6. *Ukr. Chem. J.* **1983**, *49* (5), 548−551.