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Phase Diagram for Mullite–SiF_4

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At 1 atm of SiF_4, mullite and SiF_4 react below 660° ± 7°C to form AlF_3 and SiO_2. From 660° to 1056° ± 5°C, the product is fluorotopaz. Mullite is stable in the presence of 1 atm of SiF_4 above 1056°C. The transition temperatures at other pressures of SiF_4 can be calculated from $\log p(\text{atm}) = 11.587 - 10811/T(\text{K})$ and $\log p(\text{atm}) = 9.9609 - 13238/T(\text{K})$. The phase diagram shows only gas–solid equilibria, but there is evidence for a metastable melt from which acicular mullite and fluorotopaz grow.

I. Introduction

A MIXTURE of AlF_3 and SiO_2 produces whiskers of mullite when heated to ~1200°C.[1–5] The reaction occurs in two steps, with evolution of SiF_4 at each step. Locsei[1] noted the formation of fluorotopaz at 700° ± 20°C and its decomposition to acicular mullite at 1000° ± 20°C. Talmy[2] observed these reactions at 700°–950°C and 1150°–1700°C, respectively. Abdel Rehim's DTA curves[3] indicated the formation of fluorotopaz at 760°C and mullite at 1000°C. Our thermodynamic calculations[4] predict the formation of fluorotopaz at 600°C and mullite at 1100°C under 1 atm of SiF_4. These reactions are reversible: a mixture of Al_2O_3 and SiO_2 reacts with SiF_4 to form either fluorotopaz or AlF_3, depending upon temperature and the pressure of SiF_4.[5]

Fluorotopaz made either from AlF_3 and SiO_2 or from Al_2O_3, SiO_2, and SiF_4 is a solid solution of composition $2Al_2O_3 \cdot xSiO_2 \cdot SiF_4$, where $1.07 \leq x \leq 1.53$.[6] Pyrolysis of any composition of fluorotopaz yields SiF_4 and Al_2O_3-rich mullite of composition $1.88Al_2O_3 \cdot SiO_2$.[6] The stoichiometry of these reactions can be written as

$$4AlF_3 + (3 + x)SiO_2 \leftrightarrow 2Al_2O_3 \cdot xSiO_2 \cdot SiF_4 + 2SiF_4 \quad (1)$$

$$2Al_2O_3 \cdot xSiO_2 \cdot SiF_4 \leftrightarrow 2Al_2O_3 \cdot 1.07SiO_2 + (x - 1.07)SiO_2 + SiF_4 \quad (2)$$

This chemistry can be described as a ternary system, with components Al_2O_3, SiO_2, and (2F,-O). The latter is an unusual but convenient component. The formation of the various phases from these components is described as

$$Al_2O_3 + 3(2F,\text{-}O) = 2AlF_3 \quad (3)$$

$$SiO_2 + 2(2F,\text{-}O) = SiF_4 \quad (4)$$

$$2Al_2O_3 + 2.07SiO_2 + 2(2F,\text{-}O) = 2Al_2O_3 \cdot 1.07SiO_2 \cdot SiF_4 \quad (5)$$

$$2Al_2O_3 + 2.53SiO_2 + 2(2F,\text{-}O) = 2Al_2O_3 \cdot 1.53SiO_2 \cdot SiF_4 \quad (6)$$

Proposed phase equilibria based on the literature are shown in Fig. 1. Above ~1200°C, the only stable compounds are those on the perimeter of the diagram.

One purpose of this study was to determine experimentally the dependence of the transition temperatures upon the vapor pressure of SiF_4. A second purpose was to find evidence for a liquid phase in the transition between fluorotopaz and mullite. On the basis of the morphology and stoichiometry of acicular mullite made from fluorotopaz, we have speculated[4] that the reaction involves a transient melt, despite the accepted belief that the whiskers grow by a vapor-phase process.[7–9] The variation of vapor pressure with composition would reveal a stable liquid phase, if one exists.

The contribution of species other than SiF_4 to the vapor pressure is negligible. AlF_3 and AlOF react with SiO_2 at ~600°C, according to our thermodynamic calculations,[4] where their vapor pressures are 1×10^{-6} and 1×10^{-16} atm, respectively. Si_2OF_6, obtained by reaction of SiF_4 with SiO_2, has a vapor pressure of $1.3 \times 10^{-7} P_{SiF_4}$ at 1100°C[10] and much less at lower temperatures.

II. Experimental Procedure

(1) *Preparation of Samples*

Several starting materials are available for the preparation of samples because of the reversibility of the AlF_3/fluorotopaz/mullite equilibria. The only constraint is that the samples must evolve SiF_4 during transformations.

Samples were prepared from 99.9% AlF_3 (Atomergic Chemetals Corporation, Farmingdale, NY), fused silica (Glass Grain GP-31, Harbison–Walker Refractories, Pittsburgh, PA), kaolin (Kaopaque 10, Dry Branch Kaolin Company, Dry Branch, GA), as well as fluorotopaz and κ-Al_2O_3 made in The Dow Chemical Company laboratory. The kaolin was calcined at 1000°C. Pyrolysis of kaolin at 1150°–1250°C yields mullite directly.[11,12] Therefore, the calcination was conducted at a temperature high enough to remove water but not so high as to affect mullitization.

κ-Al_2O_3 was prepared by calcining $Al(OH)_3$ (Hydral 710, Alcoa Industrial Chemicals, Bauxite, AR) at 1050°C for 1 h. Its loss on ignition by firing at 1500°C was 0.1%. Fluorotopaz was synthesized* from a commercial grade AlF_3 (Alcoa Industrial Chemicals) and fused silica. The compositions of the kaolin, $Al(OH)_3$, and Alcoa's AlF_3 are given in Table I. The AlF_3 and SiO_2 were used as if 100% pure, using the stoichiometry of Eq. (1) with $x = 4/3$. The powders were milled overnight in ethanol, dried, then milled lightly and screened through a 60 mesh sieve. The screened powder was calcined at 650°C to remove volatiles, heated slowly to 960°C, and held at that temperature for 2 h while purging with nitrogen. The vented gases were passed through a bed of $Ca(OH)_2$ to remove SiF_4. The loosely caked product was crushed by hand in a mortar and pestle and screened again.

The starting materials for each sample in this study were ground together using a mortar and pestle and screened through a 30 mesh polypropylene screen. This was done three times.

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*Synthesis of fluorotopaz was conducted by B. D. Brubaker, of The Dow Chemical Company.

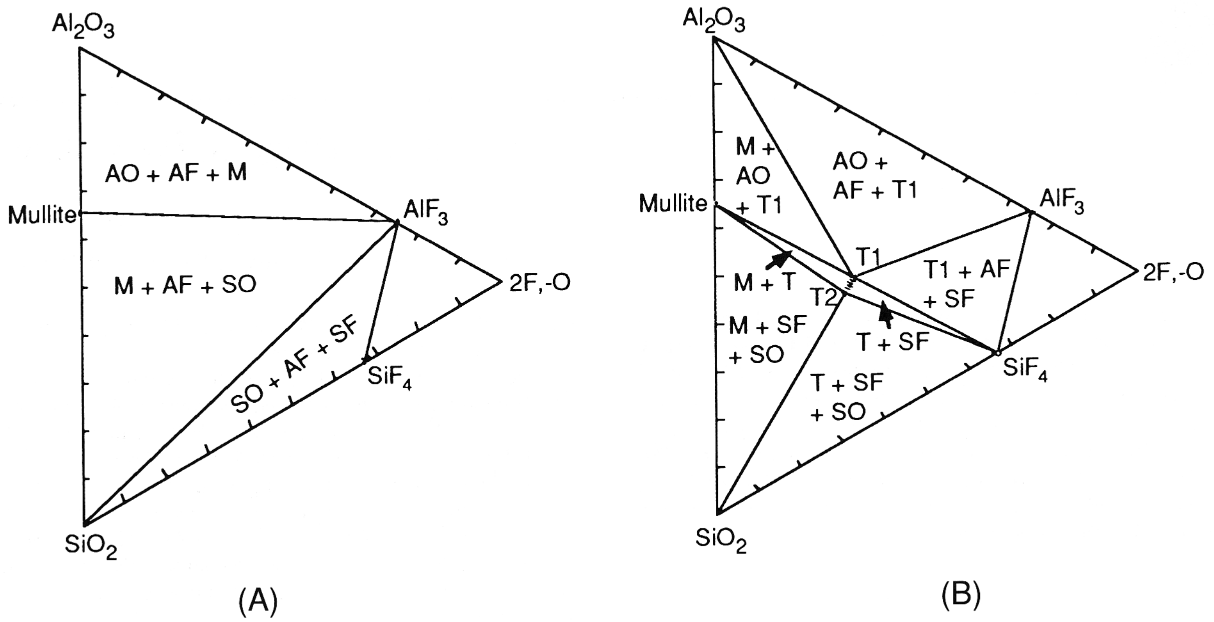

Fig. 1. Phases in the ternary system Al_2O_3–SiO_2–(2F,–O): (A) low temperature (<~600°C) and (B) high temperature (600°–900°C) (M is mullite, $1.88Al_2O_3{\cdot}SiO$; AO is Al_2O_3; AF is AlF_3; SO is SiO_2; SF is SiF_4; T1 is fluorotopaz, $2Al_2O_3{\cdot}1.07SiO_2{\cdot}SiF_4$; and T2 is fluorotopaz, $2Al_2O_3{\cdot}1.53SiO_2{\cdot}SiF_4$).

Table I. Composition of Starting Materials

Component	Composition (wt%)			
	Kaolin	$Al(OH)_3$	AlF_3	SiO_2
Al_2O_3	38.8	65.1	8.0	0.1
SiO_2	45.2	0.001	0.3	99.8
Fe_2O_3	0.3	0.007	0.03	0.02
TiO_2	0.8			
CaO	0.2			0.1
MgO	0.03			
Na_2O	0.03	0.3		0.01
K_2O	0.09			0.01
Loss on ignition	14.5	34.5		
AlF_3			88.8	
$Al_2(SO_4)_3$			0.8	
$3NaF{\cdot}AlF_3$			0.8	

The powder was pressed into 0.5 in. (1.27 cm) diameter disks using a hand-operated Carver press. The disks were broken in fragments that fitted inside a sample holder—a test tube ~7.5 cm long made from 12.5 mm diameter nickel tubing. Samples weighed 2–3 g. The sample holder was then placed inside the reactor.

(2) *The Reactor*

The reactor was a quartz test tube, 16 mm in diameter and 30 cm long. Its top was fitted with a reducing fitting (Cajon Ultra-torr®, Cajon Company, Solon, OH), which connected it to a manifold by a length of 1.5 mm diameter Teflon® (E. I. du Pont de Nemours and Company, Wilmington, DE) tubing. Attached to the manifold were a diaphragm vacuum pump (KNF Neuberger, Philadelphia, PA), a supply of nitrogen, a supply of tetrafluorosilane (Scott Specialty Gases, Plumsteadville, PA), and a pressure transducer (MKS Instruments, Andover, MA).

The reactor was mounted vertically in the center of a crucible furnace (Lindberg, Watertown, WI). The temperature inside the reactor was measured and controlled by a controller (LFE Instruments, Chesterland, OH), using a type-S thermocouple placed between the heating element and the quartz reactor. The temperature inside the reactor was determined by inserting a second type-S thermocouple inside the reactor and comparing its reading with the first thermocouple. At a setting of 750°C, the temperature inside the reactor was 746° ± 2°C over a 5 cm distance within it. At 1060°C, measured externally, the internal temperature was 1061° ± 1°C. The values cited for temperature are uncorrected values taken from the external thermocopule.

(3) *Stoichiometry of Samples*

Samples are described in terms of their formation from 3:2 mullite and SiF_4 as shown in Eqs. (7) and (8). The reverse reactions follow the stoichiometry of Eqs. (1) and (2).

$$3Al_2O_3{\cdot}2SiO_2 + 1.5SiF_4 \rightarrow 3Al_2O_3{\cdot}2SiO_2{\cdot}1.5SiF_4 \tag{7}$$

$$3Al_2O_3{\cdot}2SiO_2 + 4.5SiF_4 \rightarrow 6AlF_3 + 6.5SiO_2 \tag{8}$$

Fluorotopaz corresponds to 60 mol% SiF_4 (Eq. (7)) and AlF_3 to 81.8 mol% SiF_4 (Eq. (8)). Compositions containing 60 mol% or less of SiF_4 form fluorotopaz without evolution of SiF_4. The transition at ~600°C can be identified by this technique only in more SiF_4-rich compositions.

Two sets of samples were prepared: mixtures containing 40–60 mol% SiF_4 and those with >60 mol% SiF_4. The former were prepared from κ-Al_2O_3, kaolin, and fluorotopaz; the latter from AlF_3, kaolin, and fused silica. The actual compositions of the samples and their equivalent compositions as mole percent SiF_4 are given in Table II.

A liquid phase was introduced into some of the samples to learn its effect upon the rate of reaction. Alkali-metal and alkaline-earth-metal oxides present as impurities in the kaolin and the AlF_3 would become fluorides under our experimental conditions. A mixture of approximately equal weights of MgF_2 and LiF melts at 715°C.[13] Runs using samples containing 60 mol% SiF_4 were repeated after adding 1 and 5 wt% of the MgF_2/LiF eutectic.

This work was conducted prior to our determination of the stoichiometry of Eqs. (1) and (2). The stoichiometries of fluorotopaz and mullite were believed to be $Al_2F_2SiO_4$[14] and $3Al_2O_3{\cdot}2SiO_2$, respectively. The consequences of these assumptions is shown in Fig. 2. The composition of the samples is shown as filled circles on the join between $3Al_2O_3{\cdot}2SiO_2$ and SiF_4. The reactions between $3Al_2O_3{\cdot}2SiO_2$ and SiF_4 yielded fluorotopaz of varying composition. Our observation that the vapor pressure of the system was independent of composition shows that these departures from precise stoichiometry had no effect upon the measured vapor pressures.

(4) *Determination of Vapor Pressure*

Samples were heated at 400°C under vacuum for 1–2 h to remove moisture. The furnace temperature was set to a reaction

Table II. Composition of Samples

SiF_4 (mol%)	Composition (wt%)				
	Al_2O_3	AlF_3	Kaolin	SiO_2	Fluorotopaz
39.5	23.43	0	26.2	0	50.38
50.2	12.74	0	14.24	0	73.02
55.2	6.66	0	7.44	0	85.60
60.0	0	0	0	0	100
69.6	0	33.6	43.6	16.3	0
81.8	0	56.38	0	43.62	0

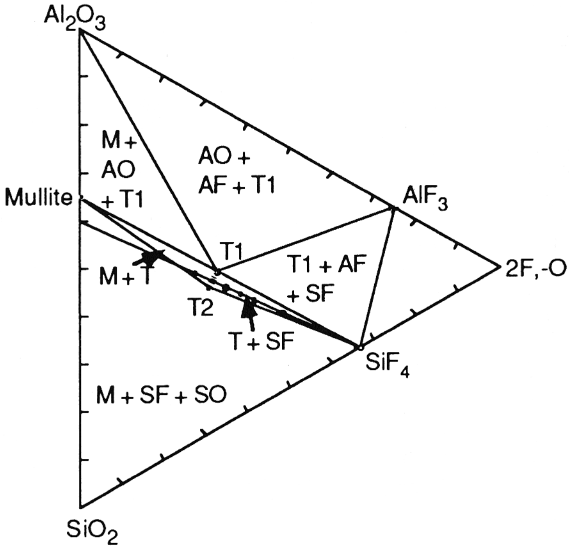

Fig. 2. Composition of samples (solid circles) (M is mullite, $1.88Al_2{\cdot}O_3{\cdot}SiO$; AO is Al_2O_3; AF is AlF_3; SO is SiO_2; SF is SiF_4; T1 is fluorotopaz, $2Al_2O_3{\cdot}1.07SiO_2{\cdot}SiF_4$; and T2 is fluorotopaz, $2Al_2O_3{\cdot}1.53SiO_2{\cdot}SiF_4$).

temperature of ~600°C. The pressure within the reactor was recorded versus time until it reached a constant value. The temperature was then increased and the process was repeated. The equilibrium vapor pressure of each composition was determined at three different temperatures. The pressure at 1 atm was calculated by extrapolating a plot of log P versus the reciprocal of the absolute temperature (Clausius–Claperyon equation).

The sample was then converted completely to fluorotopaz by heating at ~800°C until the evolution of SiF_4 ceased. It was then evacuated and set at a reaction temperature for the conversion of fluorotopaz to mullite.

The reaction between AlF_3 and fused silica at 600°–650°C to form fluorotopaz is extremely slow. The vapor pressure of the samples containing >60 mol% SiF_4 did not reach a steady state in more than a week at 650°C. Instead, the reactor was heated to 720°–750°C until the vapor pressure of SiF_4 reached or exceeded 1 atm. The furnace temperature was then decreased, and the reactor and its contents were allowed to reach thermal equilibrium. Pressure versus time was observed for a few hours. If the pressure decreased, a little of the SiF_4 was pumped off to reduce the pressure and the observation was repeated. The process was continued until the pressure remained constant for 4 h. This temperature was recorded as the equilibrium vapor pressure at that temperature. The process was repeated at two other temperatures.

III. Results

The rate of evolution of SiF_4 at three temperatures for a composition containing 50.2 mol% SiF_4 is shown in Fig. 3. The rate of evolution of gas approaches zero as the pressure approaches the equilibrium value. The assumption that the rate is proportional to the difference between the pressure, P, and the equilibrium value, P_{eq}, is expressed as

$$\frac{dP}{dt} = k(P_{eq} - P) \tag{9}$$

This integrates to

$$P = P_{eq} - (P_{eq} - P_0)e^{-kt} \tag{10}$$

where P_0 is the pressure at $t = 0$. The dashed curves in Fig. 3 show the fit of the data to Eq. (10). All of the experimental data for the transition from fluorotopaz to mullite and SiF_4 were fitted to Eq. (10). The results are summarized in Table III.

The kinetic data for the fluorotopaz–mullite transition do not show a consistent pattern. Any dependence of rate upon temperature is obscured by other factors. Typically, the first reaction of any sample, usually at 990°C, was the fastest.

The temperature dependence of the equilibrium vapor pressure shown in Fig. 3 is given in Fig. 4, a plot of log P_{eq} versus the reciprocal of the absolute temperature. The transition temperature for this composition is determined to be 1059°C. The results of similar extrapolations from the data in Table III are given in Table IV. The temperature dependence of the vapor pressure of fluorotopaz using the combined data is

$$\log p(\text{atm}) = 9.9609 - 13238/T(\text{K}) \tag{11}$$

The average value for the fluorotopaz–mullite transition temperature, under a pressure of 1 atm of SiF_4, is 1056° ± 5°C. For $P_{SiF_4} = 0.1$ atm, the equilibrium occurs at 935°C.

The temperatures and pressures at which samples containing >60 mol% SiF_4 reached equilibrium (Eq.(1)) are given in Table V. Their extrapolation to determine the temperature at which $P_{eq} = 1$ atm is shown in Fig. 5. The temperature dependence of the pressure of SiF_4 in equilibrium with AlF_3, SiO_2, and fluorotopaz (Eq. (1)) is

$$\log p(\text{atm}) = 11.587 - 10811/T(\text{K}) \tag{12}$$

The average of the two determinations is 660°C, with an estimated error of ±7°C. For $P_{SiF_4} = 0.1$ atm, the equilibrium occurs at 584°C. The reaction in both directions is very slow at these temperatures.

The transition temperatures are plotted versus composition in the phase diagram shown in Fig. 6.

We sought visual evidence for a melt in two ways. First, mullite was exposed to SiF_4 at a pressure of 600 torr (78 kPa) and ~1000°C, then slowly cooled. The melt could exist only until fluorotopaz nucleated. The result is shown in Fig. 7. The mullite whiskers are coated with a melt that has formed beads in some places and that has formed starbursts of the stable phase, fluorotopaz, near the bottom of the micrograph. Second, a pyrolysis of fluorotopaz at ~1000°C was interrupted.[†] The product is shown in Fig. 8. The small crystals are fluorotopaz. The large crystal of mullite is coated with a liquid.

IV. Phase Diagram

The phase diagram contains two horizontal lines. The lower, at 660°C, represents the transition temperature for Eq. (1), the

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[†] Pyrolysis of fluorotopaz and micrograph by B. D. Brubaker, The Dow Chemical Company laboratory.

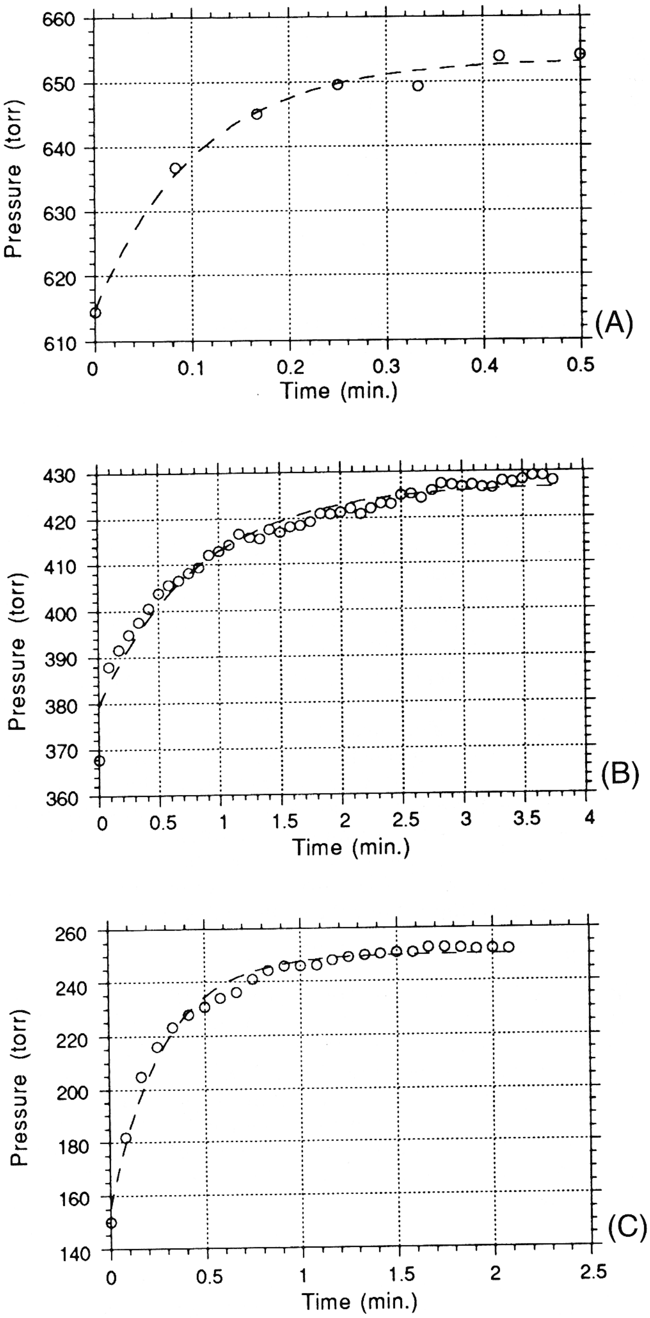

Fig. 3. Rate of reaction for 50.2 mol% SiF_4 at (A) 1050°, (B) 1020°, and (C) 990°C.

equilibrium between AlF_3 (plus SiO_2) and fluorotopaz. The transition from fluorotopaz to mullite (Eq. (2)) is represented by the horizontal line at 1056°C. The vertical lines correspond to the stoichiometries of fluorotopaz and AlF_3, as shown in Eqs. (7) and (8). The transition temperatures for pressures other than 1 atm can be calculated from Eqs. (11) and (12).

The Al_2O_3–SiO_2 system has a metastable eutectic at 1260°C, with a composition ~12 mol% SiO_2.[15] This is represented by a small open circle on the y-axis. The melt exists only in the absence of mullite. This melt has been proposed as intermediate in the reaction between α-Al_2O_3 and SiO_2 to form mullite.[17–19]

V. Discussion

Table III. Summary of Experimental Data for Fluorotopaz → Mullite + SiF_4

SiF_4 (mol%)	T (°C)	P_{eq} (torr)*	P_0 (torr)*	k
39.5	990	201	9	15.75
39.5	1020	392	343	1.18
39.5	1050	700	597	1.81
50.2	990	253	150	2.3
50.2	1020	427	398	
50.2	1050	653	615	9.42
50.2	990	295	211	6.07
50.2	1020	480	420	1.31
50.2	1050	782	721	2.13
55.2	990	220	63	2.53
55.2	1020	386	303	1.32
55.2	1040	568	368	2.44
55.2	1040	587	446	1.26
60.0	990	222	75	2.8
60.0	990	252	125	3.2
60.0	990	295	87	4.77
60.0	1020	390	321	0.77
60.0	1050	647	420	0.70
60.0†	990	196	20	0.13
60.0†	990	199	80	0.16
60.0†	1020	375	220	0.70
60.0†	1050	736	425	0.20
60.0‡	990	222	140	3.1
60.0‡	990	251	125	3.0
60.0‡	1020	374	150	1.12
60.0‡	1020	393	320	2.18
60.0‡	1050	591	200	0.73
60.0‡	1050	658	235	1.28

*1 torr = 1.3×10^2 Pa. †Plus 1 wt% MgF_2/LiF eutectic. ‡Plus 5 wt% MgF_2/LiF eutectic.

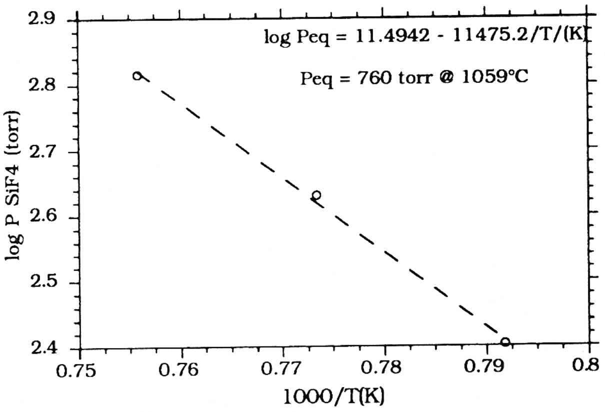

Fig. 4. Temperature dependence of the equilibrium vapor pressure of 50.2 mol% SiF_4.

Despite the visual evidence for a molten phase in this system, the phase diagram indicates that a stable melt in this system is not permitted by the phase rule. For this system, $F = C - P + 1$, because temperature and pressure are not independently variable. In the regions where only solid phases are present, temperature and pressure are linked by Eqs. (11) or (12). Where the vapor phase exists in Fig. 6, the pressure is 1 atm for all temperatures. The phase rule for a three-component system (SiO_2–Al_2O_3–(2F,-O)) with one degree of freedom permits three phases at equilibrium. Our observation that the vapor pressure of fluorotopaz is independent of composition shows that the system has just one degree of freedom when mullite, fluorotopaz, and SiF_4 are in equilibrium. A liquid phase is therefore possible only in the absence of one of the stable solid phases; i.e., only a metastable liquid is possible.

The melting point of a ternary metastable eutectic in the system SiO_2–Al_2O_3–SiF_4 should be <1260°C, the melting point of the binary eutectic in the Al_2O_3–SiO_2 system.[15] Its metastability, with respect to fluorotopaz, requires that the vapor pressure of SiF_4 in equilibrium with this melt be higher than that of fluorotopaz. Its representation on the phase diagram can be

Table IV. Temperatures at which Fluorotopaz and Mullite Equilibrate with 1 atm of SiF_4*

SiF_4 (mol%)	a	b	T (K)	T (°C)
39.5	14.2792	−15 121.3	1327	1054
50.2	11.494	−11 475	1332	1059
50.2	11.8177	−11 809.3	1321	1048
55.2	14.100	−14 910	1329	1056
60.0	11.218	−11 134	1335	1062
Average				1056 ± 5

*$\log P_{eq} = a + b/T(\mathrm{K})$.

Table V. Summary of Experimental Data for $AlF_3 + SiO_2 \rightarrow$ Fluorotopaz + SiF_4

SiF_4 (mol%)	T (°C)	P_{eq} (torr)*
69.6	610	141
69.6	650	504
69.6	660	722
81.8	610	165
81.8	610	225
81.8	640	460
81.8	650	750
81.8	660	720

*1 torr = 1.3 × 10^2 Pa.

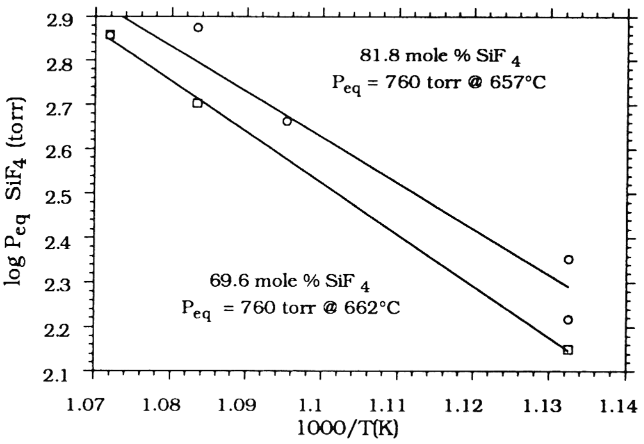

Fig. 5. Temperature dependence of the equilibrium vapor pressure of 69.6 and 81.8 mol% SiF_4.

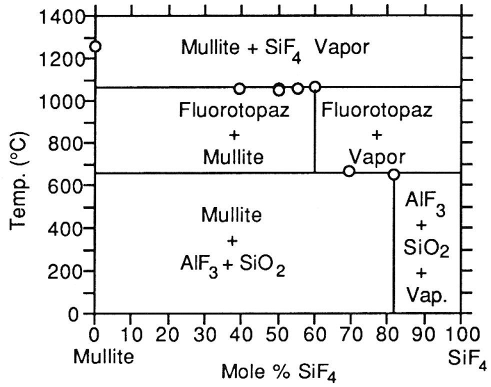

Fig. 6. System mullite–SiF_4 at 1 atm. System is pseudobinary below 1056°C with four components (mullite, AlF_3, SiO_2, and SiF_4).

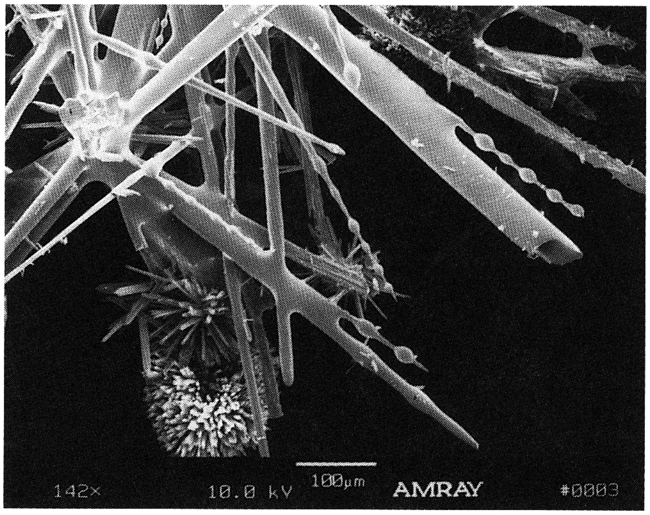

Fig. 7. Melt from cooling acicular mullite in 1 atm of SiF_4.

hypothesized as a horizontal line that intercepts the y-axis below 1056°C. In an earlier study,[4] we reported a dramatic increase in the rate of decomposition of fluorotopaz between 975° and 993°C. That increase may identify the intercept at pressures approaching 1 atm of SiF_4.

VI. Summary

At 1 atm of SiF_4 and 660° ± 7°C, fluorotopaz equilibrates very slowly with a mixture of AlF_3 and SiO_2. Mullite and SiF_4, at 1 atm, are in equilibrium at 1056° ± 5°C with fluorotopaz. Both transition temperatures are independent of composition. The rate of formation of mullite from fluorotopaz is proportional to $P - P_{eq}$, is independent of temperature, and is unaffected by addition of a molten phase. The pressure of SiF_4 in

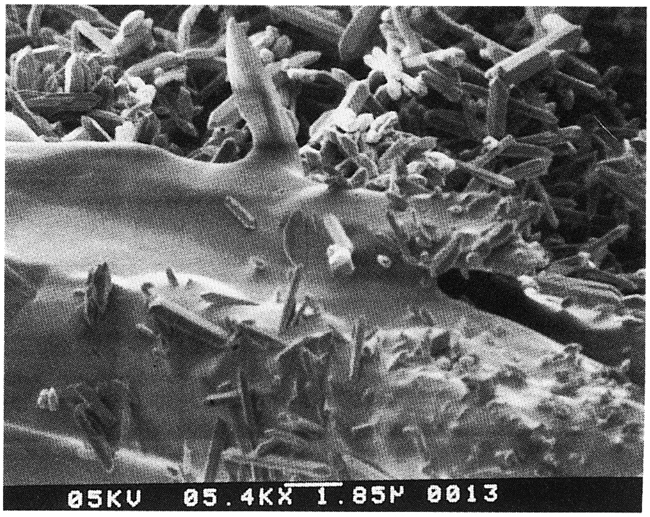

Fig. 8. Incomplete pyrolysis of fluorotopaz showing metastable melt.

equilibrium with fluorotopaz and mullite is log p(atm) = 9.9609 − 13238/T(K). The equilibrium vapor pressure of a mixture of AlF_3, SiO_2, and fluorotopaz is log p(atm) = 11.587 − 10811/T(K).

The phase diagram shows a vapor–solid equilibrium. There is evidence that mullite and fluorotopaz grow from a metastable melt that is derived from the metastable eutectic in the Al_2O_3–SiO_2 system (~12 mol% Al_2O_3; melting point of 1260°C) by addition of SiF_4.

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References

[1] B. Locsei, "Contributions to the Kinetics of Mullite Formation in the System Aluminum Fluoride–Silica I," *Acta Chim. Hung.*, **33**, 198–210 (1962).

[2] I. G. Talmy and D. A. Haught, "Mullite Whisker Preparation," U.S. Pat. No. 4 911 902, Mar. 27, 1990 and U.S. Pat. No. 4 948 766, Aug. 14, 1990.

[3] A. M. Abdel Rehim, "Formation of Mullite, Topaz, and Corundum," *Thermochim. Acta*, **13**, 231–39 (1975).

[4] J. R. Moyer, M. S. LaBarge, B. D. Brubaker, and N. N. Hughes, "Kinetics and Mechanism of Formation of Mullite Whiskers," *Mater. Sci. Monogr.*, **68**, 57–66 (1991).

[5] J. R. Moyer and N. N. Hughes, "A Catalytic Process for Mullite Whiskers," *J. Am. Ceram. Soc.*, **77** [4] 1083–86 (1994).

[6] J. R. Moyer and P. R. Rudolf, "Stoichiometry of Fluorotopaz and of Mullite Made from Fluorotopaz," *J. Am. Ceram. Soc.*, **77** [4] 1087–89 (1994).

[7] K. Okada and N. Ōtsuka, "Synthesis of Mullite Whiskers by Vapour-Phase Process," *J. Mater. Sci. Lett.*, **8**, 1052–54 (1989).

[8] M. G. U. M. Ismail, H. Arai, Z. Nakai, and T. Akiba, "Mullite Whiskers from Precursor Gel Powders," *J. Am. Ceram. Soc.*, **72** [9] 2736–39 (1990).

[9] K. Okada and N. Ōtsuka, "Synthesis of Mullite Whiskers and Their Application in Composites," *J. Am. Ceram. Soc.*, **74** [10] 2414–18 (1991).

[10] M. Shinmei, T. Imai, and T. Yokokawa, "Thermodynamic Study of Si_2OF_6 from 723 to 1288 K by Mass Spectrometry," *J. Chem. Thermodyn.*, **18**, 241–46 (1986).

[11] J. F. Duncan and K. J. D. Mackenzie, "Kinetics and Mechanisms of High-Temperature Reactions of Kaolinite Minerals," *J. Am. Ceram. Soc.*, **52** [2] 74–77 (1990).

[12] A. K. Chakravorty and D. K. Ghosh, "Kaolinite–Mullite Reaction Series: The Development and Significance of a Binary Aluminosilicate Phase," *J. Am. Ceram. Soc.*, **74** [6] 1401–406 (1991).

[13] P. P. Pedotieff and K. Timofeev, Fig. 1461 in *Phase Diagrams for Ceramists*, Vol. 1. Edited by E. M. Levin, C. R. Robbins, and H. F. McMurdie. American Ceramic Society, Columbus, OH, 1964.

[14] M. D. Barton, H. T. Haselton Jr., B. S. Hemingway, O. J. Kleppa, and R. A. Robie, "The Thermodynamic Properties of Fluorotopaz," *Am. Mineral.*, **67** [3,4] 350–55 (1982).

[15] S. H. Risbud and J. A. Pask, "SiO_2–Al_2O_3 Metastable Phase Equilibrium Diagram without Mullite," *J. Mater. Sci.*, **13**, 2449–54 (1978).

[16] B. Sonuparlak, "Sol–Gel Processing of Infrared Transparent Mullite," *Adv. Ceram. Mater.*, **3** [3] 263–67 (1988).

[17] T. J. Mroz, "Microstructural Evolution of Mullite Formed by Reaction Sintering of Sol–Gels"; M.S. Thesis. Department of Ceramic Engineering, Alfred University, Alfred, NY, 1988.

[18] A. J. Skoog and R. E. Moore, "Refractory of the Past for the Future: Mullite and Its Use as a Bonding Phase," *Am. Ceram. Soc. Bull.*, **67** [7] 1180–85 (1988). ☐