The thermodynamic properties of fluor-topaz

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Abstract

The standard thermodynamic properties of fluor-topaz, $Al_2SiO_4F_2$, have been calculated from low- and high-temperature heat-capacity measurements and from high-temperature, oxide-melt calorimetry. Fluor-topaz (from Topaz Mountain, Thomas Range, Utah) containing 0.04 wt. percent water was used in all the experiments. Adiabatic calorimetry performed from 10.6 to 379.2 K gives $S_{298}^{\circ} - S_0^{\circ}$ of 105.4 ± 0.2 J/mol·K. Combined heat capacities determined by adiabatic calorimetry (200–380 K) and differential scanning calorimetry (340–800 K) were fit to the following polynomial (equation valid 200–1,000 K):

$$C_p^{\circ} \text{ (J/mol·K)} = 471.41 - 0.08165T + 1.2695 \times 10^6 T^{-2} - 5485.5T^{-0.5} \ (\pm 0.7\%).$$

The enthalpy of the reaction $CaF_2 + Al_2O_3 + SiO_2 = CaO + Al_2SiO_4F_2$ was measured at 970 K by oxide-melt calorimetry and gave $\Delta H_{970}^{\circ} = 91.88 \pm 3.56$ kJ. From our heat-capacity measurements and ancillary data, we calculate $\Delta H_{298}^{\circ} = 96.12 \pm 3.95$ kJ for the reaction and $\Delta H_{f,298}^{\circ} = -3084.45 \pm 4.70$ kJ/mol, and $\Delta G_{f,298}^{\circ} = -2910.66 \pm 4.74$ kJ/mol for fluor-topaz.

Introduction

Topaz occurs frequently as an accessory mineral in fluorine-rich granitic rocks and associated hydrothermally altered rocks. As one of the principal fluorine bearing minerals, it offers a key to understanding the genesis of these rocks. Topaz is a solid solution between fluor-topaz ($Al_2SiO_4F_2$) and (hypothetical) hydroxyl-topaz ($Al_2SiO_4(OH)_2$). Natural topazes vary from nearly pure fluor-topaz to about $Al_2SiO_4F_{1.4}(OH)_{0.6}$, although Rosenberg (1972) has synthesized topaz containing more than 50% hydroxyl-topaz component.

Rosenberg (1972, 1978) reported synthesis results involving topaz solid solutions; his is the only work from which thermodynamic data might be derived. This study was undertaken to measure the thermodynamic properties of fluor-topaz as part of a project on the thermochemistry of topaz and other fluoro-silicates and their petrological application.

Experimental methods and results

Starting materials

Natural fluor-topaz from Topaz Mountain, Thomas Range, Juab County, Utah, was collected

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from the Pliocene topaz-rich alkali rhyolites (Lindsey, 1979). This topaz is known to be very close to the fluorine end member (Penfield and Minor, 1894; Ribbe and Rosenberg, 1971) and occurs as crystals as large as 3 cm in the rhyolite lithophysae. Associated minerals include quartz, sanidine, plagioclase, biotite, fluorite, beryl, hematite, pseudobrookite, spessartine, and bixbyite (Ream, 1979). About 60 g of transparent, inclusion-free crystals and cleavage fragments were handpicked from a few hundred grams of rough material. Approximately one-third of the crystals were light brown; this color is apparently caused by electronic defect centers (Dickinson and Moore, 1967), not chemical impurities. As previously demonstrated (*e.g.*, Nassau and Prescott, 1975), the color is removed by heating to 500°C for several hours. We did not heat treat the material used for calorimetry. We did not attempt to synthesize fluor-topaz by the reaction $2AlF_3 + 2Al_2O_3 + 3SiO_2 = 3Al_2SiO_4F_2$ nor did we attempt to use this reaction for the solution calorimetry because of the tendency of AlF_3 to hydrolyze which could result in considerable uncertainty as to the compositions of the phases under study.

Several crystals were analyzed on an automated electron microprobe at the University of Chicago using a ZAF correction program written by I. M. Steele of the University of Chicago. The beam current was 15 ma at an accelerating voltage of 15 kv. Andalusite served as the standard for aluminum and silicon. The water and fluroine were analyzed at the U. S. Geological Survey with a Perkin Elmer 240B elemental analyzer (V_2O_5 flux) and a specific ion electrode respectively. The water and fluorine analyses on this material are in good agreement with the original analyses by Penfield and Minor (1894). Although we searched for other elements, none were detected. Crystallographic data were collected using powder-diffraction methods (Ni-filtered $CuK\alpha$ radiation with a corundum internal standard $a = 0.47593(1)nm$, $c = 1.29917(5)nm$. The program of Burnham (1962) was used to refine the data. The chemical and crystallographic data are given in Table 1.

Other materials used in the high-temperature oxide-melt calorimetry were CaO (prepared from reagent $CaCO_3$, sintered at 1,400°C for 1 week); optically pure natural CaF_2 (southern Illinois, University of Chicago collection #1875); optically pure natural quartz (locality unknown, University of Chicago collection #2099); and α-Al_2O_3 (prepared from reagent $Al(OH)_3$, fired at 1,300°C for 2 days).

Adiabatic calorimetry

Heat-capacity measurements were made from 10.6 to 379.2 K by adiabatic calorimetry at the U.S. Geological Survey, Reston, Virginia. The cryostat and calorimeter have been described in detail by Robie and Hemingway (1972) and Robie *et al.* (1976).

The topaz sample (50.5654 g, corrected for buoyancy) was loaded into the calorimeter. After evacuation of air from the calorimeter, it was backfilled with dry helium gas at 6×10^3 pascals pressure (4.0×10^{-5} mole of He) to promote thermal equilibration, and sealed. The reported temperatures refer to the International Practical Temperature Scale of 1968 (IPTS-68).

Table 2 gives the results, corrected for curvature, for the four series (1–4) of experiments in their order of collection. The formula weight for pure fluor-topaz of 184.043 g/mol used in the calculations is based on the 1975 values for the atomic weights (Commission on Atomic Weights, 1976). Although the sample topaz contains 0.04 weight percent OH, no correction was made to the measured heat capacities because the heat capacity of hydroxyl-topaz is not known. From comparisons of the heat capacities of hydroxyl-apatite and fluor-apatite, and those of hydroxyl-phlogopite and fluorphlogopite, we estimate that the difference in the heat capacity between fluor- and hydroxyl-topaz would not exceed approximately 7 percent. The difference in $S_{298}^\circ - S_0^\circ$ between hydroxyl-apatite and fluor-apatite is 0.6 percent, and between hydroxyl-phlogopite and fluor-phlogopite is -0.5 percent. On the basis

Table 1. Chemical and crystallographic data

	Chemistry*		Cell Parameters
	Oxide wt %	Moles**	
Al_2O_3	56.08	1.00	a = 0.46475(3) nm
SiO_2	32.74	0.99	b = 0.87897(4) nm
F	20.3	1.95	c = 0.83920(4) nm
H_2O	0.04	0.01†	V = 0.34281(2) nm³
	———		
Total	109.16		
Less F = O	100.61		

* Al and Si analyses by microprobe, F by specific ion electrode, and H_2O by CHN elemental analyzer.

** Based on 5 oxygens.

† As hydroxyl.

of the above observations, we estimate that the correction to the measured entropy of our sample, caused by the replacement of 10 percent (10 times what is actually present) of the fluorine by hydroxyl, would be less than 0.1 percent, which is somewhat less than our experimental uncertainty. Figure 1 shows the measured heat capacities.

Differential scanning calorimetry

Heat capacity measurements were made from 340 to 800 K with a differential scanning calorimeter at the U. S. Geological Survey. A cleavage flake of topaz weighing 25 mg placed in an unsealed gold pan was used. The data were collected and reduced using a computer program written by K. M. Krupka of Batelle Northwest Laboratories, which utilizes scans made with a corundum disk over the same temperature intervals as the unknown. The heat capacities given by Ditmars and Douglas (1971) for corundum were used in the reduction. Additional details of the experimental method are given by Krupka et al. (1979). Because of difficulties with instrument stability, reliable data could not be obtained at temperatures greater than 800 K. The data are given in Table 2, series 5–9, and are plotted in Figure 1.

Enthalpy of solution measurements

High temperature oxide-melt calorimetry was used to determine the enthalpy of formation of fluor-topaz according to the reaction:

$$Al_2O_3 + SiO_2 + CaF_2 = Al_2SiO_4F_2 + CaO \quad (1)$$
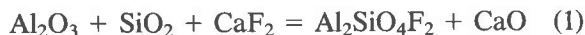
Enthalpy of solution values were obtained for CaO, $Al_2SiO_4F_2$, CaO + $Al_2SiO_4F_2$ (molar 1:1 mixture), and CaF_2 + Al_2O_3 + SiO_2 (molar 1:1:1 mixture) and

Table 2. Experimental heat capacities for fluor-topaz. Formula weight 184.043 g/mol.

Temp. K	Heat capacity J/(mol·K)	Temp. K	Heat capacity J/(mol·K)	Temp. K	Heat capacity J/(mol·K)
Series 1		Series 3		Series 6	
305.57	146.3	243.81	121.7	470.7	187.3
310.27	148.0	249.36	124.0	480.7	188.9
315.93	149.7	254.89	126.4	490.7	190.5
321.48	151.4	260.41	129.1	500.6	192.2
327.31	153.5	265.91	131.3	510.6	193.3
333.12	155.3	271.40	133.4	520.6	194.5
338.92	156.7	276.87	135.7	530.6	196.1
344.72	158.3	282.34	137.8	540.6	196.1
350.49	160.2	287.79	139.7	550.6	198.0
356.26	162.0	293.23	142.0	560.5	199.2
362.02	163.0	298.65	144.0	570.5	200.8
367.77	164.4	304.07	145.8	580.5	200.9
373.50	166.3	309.47	147.6	590.5	201.8
379.21	167.7	314.87	149.4	600.5	202.9
Series 2		320.25	150.9		
54.20	6.547	Series 4		Series 7	
60.48	8.687	10.66	0.0189	770.2	213.3
65.10	11.44	11.77	0.0261	780.2	213.1
70.54	14.92	12.99	0.0356	790.2	215.2
76.80	18.63	14.33	0.0538	800.2	215.6
82.86	22.23	15.85	0.0768		
89.02	26.11	17.54	0.1141	Series 8	
95.18	30.19	19.42	0.1691	470.7	187.1
101.29	34.31	21.52	0.2400	480.7	188.5
107.36	38.49	23.87	0.3411	490.7	189.8
113.40	42.63	26.49	0.4993	500.7	191.1
119.40	46.81	29.43	0.7533	510.6	191.7
125.37	51.06	32.73	1.215	520.6	192.7
131.32	55.18	36.41	1.822	530.6	193.9
137.24	59.25	40.56	2.723	540.6	194.7
143.14	63.22	45.22	3.982	550.6	196.0
149.02	67.12	50.44	5.527	560.5	197.1
Series 3		56.27	7.120	570.5	197.7
154.82	71.30	62.56	9.836	580.5	198.8
160.46	74.92	Series 5		590.5	200.1
165.70	78.36	570.5	199.0	600.5	203.0
171.04	81.73	580.5	200.0		
176.71	85.21	590.5	200.8	Series 9	
182.35	88.84	600.5	201.5	340.0	157.5
187.98	92.09	610.4	202.9	350.0	159.6
193.61	95.40	620.4	203.7	360.0	161.4
199.23	98.51	630.4	204.3	370.0	163.9
204.82	101.5	640.4	204.8	380.0	166.3
210.42	104.9	650.4	205.1	390.0	169.0
216.00	108.0	660.4	205.4	400.0	171.3
221.58	110.5	670.3	206.3	410.0	173.3
227.14	113.2	680.3	207.6	420.0	175.0
232.70	116.3	690.3	207.0	430.0	176.6
238.25	119.1	700.3	209.7	440.0	179.1
				450.0	181.3
				460.0	183.2
				470.0	185.0
				480.0	187.0
				490.0	189.2
				500.0	191.2
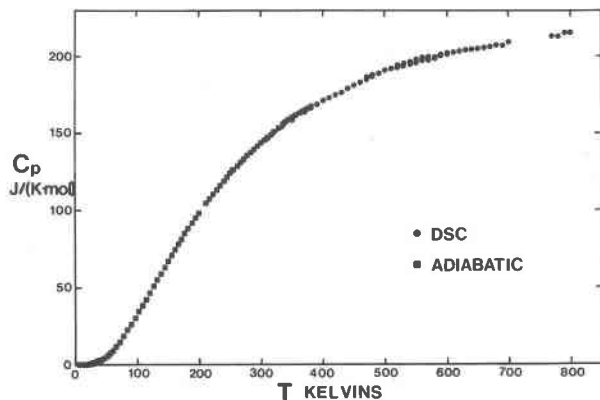
are given in Table 3. Attempts to measure the enthalpy of solution of pure CaF_2 failed due to sintering of the powder which prevented complete dissolution during the time of the experiments (50 minutes). Westrich and Navrotsky (1981) encountered similar problems with the dissolution of fluorite.

The calorimetric methods have been described recently by Charlu et al. (1978). Heat-treated

Fig. 1. Experimental heat capacities for fluor-topaz.

Table 3. Enthalpy of solution measurements

Material	ΔH_{970}^{o} kJ	Experimental data in chronological order ΔH_{970}^{o} (kJ/mol); Sample wt (mg) in parentheses
$Al_2SiO_4F_2$	$76.57 \pm 1.67^{*}$	74.74(29.88), 74.21(44.77), 79.68(41.84), 80.16(47.96) 72.46(41.28), 78.64(35.32), 80.39(50.80), 71.54(28.32) 74.56(37.60), 78.04(42.71), 78.88(36.29), 79.53(24.50)
CaO	-55.06 ± 4.10	-62.10(13.78), -57.59(12.71), -54.30(10.44), -45.68(15.11) -49.97(16.22), -64.68(14.50), -63.32(13.10), -48.54(15.44) -60.33(13.06), -50.11(13.99), -49.02(14.85)
$CaO + Al_2SiO_4F_2$	29.83 ± 3.05	20.96(29.58), 29.19(26.69), 38.67(34.10), 31.67(56.75) 29.01(50.10), 26.60(47.48), 28.81(66.64), 39.10(50.63) 29.48(45.00), 23.11(53.18), 32.37(73.24), 29.25(44.86)
$CaF_2 + Al_2O_3 + SiO_2$	121.71 ± 1.80	121.33(30.00), 122.31(30.74), 124.72(36.39), 118.52(30.50) 121.21(30.50), 127.65(38.90), 122.20(40.78), 120.26(46.13) 120.35(40.79), 117.79(39.05), 118.32(40.45)
addition of CaO to $Al_2SiO_4F_2$	21.51 ± 4.44	
$CaF_2 + Al_2O_3 + SiO_2 = CaO + Al_2SiO_4F_2$	$\Delta H_{970}^{o} {}^{**}= 91.88 \pm 3.56$ kJ $\Delta H_{298}^{o} = 96.12 \pm 3.95$ kJ	

* Two standard errors of the mean; errors are propagated assuming they are independent; possible systematic errors have been neglected.
** Using the value for the mechanical mix of CaO + Al2SiO4F2; see text.

$Pb_2B_2O_5$ glass from a single homogeneous batch was used in all the experiments. The topaz, CaO, Al_2O_3, SiO_2, and CaF_2 were sized to -150 to $+350$ mesh and kept in a desiccator.

A 2 month exposure to air in the desiccator reduced the heat of solution of CaO by about 10 percent, apparently because of the formation of small amounts of $Ca(OH)_2$ and/or $CaCO_3$. Brief heating to 1,300°C before each experiment eliminated this perturbation. The final value obtained for ΔH_{soln} at 970 K of CaO in this study (-55.06 kJ/mol) agrees very well with that reported by Newton *et al.* (1977) (-55.15 kJ/mol). None of the other materials showed a time dependence in their heat effects. In addition, consecutive measurements on the same material in a given batch of melt showed no significant variation with increasing concentration of solute. In no series of experiments,

however, was more than 200 mg of material dissolved in any given 30.5 g batch of melt.

Two different values were obtained for the heat of solution of the $Al_2SiO_4F_2$ + CaO. The linear combination of the heat of solution of $Al_2SiO_4F_2$ and the heat of solution of CaO (21.5 ± 4.44 kJ/mol) differs significantly from the heat of solution for the mechanical mixture (29.83 ± 3.05 kJ/mol). Consecutive dissolution experiments of stoichiometric proportions of $Al_2SiO_4F_2$ followed by pure CaO in the same alliquot of melt confirmed the mechanical-mixture value. Therefore, the value of the mechanical mixture is used in the evaluation of the enthalpy of fluor-topaz. We have considered the effect of systematic errors, including those resulting from hydrolysis (of topaz, CaF_2, CaO), reaction of the mechanical mixture before the experiments, and impurities (*e.g.*, 0.04 percent H_2O in the topaz).

Table 4. Smoothed thermodynamic properties for $Al_2SiO_4F_2$

TEMP.	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	$C_p^\bullet$	$(S_T^\bullet - S_0^\bullet)$	$(H_T^\bullet - H_0^\bullet)/T$	$-(G_T^\bullet - H_0^\bullet)/T$
KELVIN		J/(mol·K)		
5	0.002	0.001	0.002	0.001
10	0.015	0.005	0.004	0.001
15	0.063	0.018	0.014	0.004
20	0.188	0.051	0.040	0.011
25	0.403	0.113	0.088	0.025
30	0.822	0.219	0.171	0.048
35	1.575	0.400	0.316	0.084
40	2.588	0.672	0.533	0.140
45	3.919	1.052	0.833	0.219
50	5.391	1.541	1.215	0.326
60	8.495	2.775	2.148	0.627
70	14.56	4.521	3.471	1.050
80	20.52	6.858	5.232	1.625
90	26.75	9.628	7.271	2.357
100	33.44	12.79	9.552	3.239
110	40.29	16.30	12.03	4.264
120	47.25	20.10	14.68	5.424
130	54.28	24.16	17.45	6.707
140	61.11	28.44	20.33	8.106
150	67.87	32.88	23.27	9.608
160	74.66	37.48	26.27	11.21
170	81.07	42.20	29.31	12.89
180	87.33	47.01	32.36	14.65
190	93.30	51.89	35.41	16.48
200	98.92	56.82	38.45	18.38
210	104.6	61.79	41.46	20.33
220	109.8	66.78	44.45	22.32
230	114.8	71.77	47.40	24.36
240	119.9	76.76	50.32	26.44
250	124.3	81.75	53.19	28.56
260	128.8	86.71	56.01	30.70
270	132.9	91.65	58.79	32.86
280	136.9	96.56	61.51	35.05
290	140.7	101.4	64.17	37.26
300	144.4	106.3	66.78	39.48
310	147.8	111.0	69.34	41.71
320	151.0	115.8	71.84	43.95
330	154.3	120.5	74.29	46.20
340	157.1	125.1	76.69	48.45
350	160.0	129.7	79.02	50.71
360	162.7	134.3	81.31	52.97
370	165.2	138.8	83.54	55.22
380	168.0	143.2	85.73	57.48
400	172.4	152.0	89.9	62.1
450	182.3	172.9	99.7	73.2
500	190.3	192.5	108.3	84.2
550	196.8	211.0	116.2	94.8
600	202.0	228.3	123.1	105.2
650	206.2	244.7	129.3	115.4
700	209.5	260.1	134.9	125.2
750	212.1	274.6	140.0	134.6
800	214.1	288.4	144.5	143.9
850	215.6	301.4	148.7	152.7
900	216.6	313.8	152.5	161.3
950	217.3	325.5	155.8	169.7
1000	217.6	336.6	159.0	177.6
273.15	134.5	93.20	59.65	33.55
298.15	144.0	105.4	66.30	39.06

Table 5. Standard thermodynamic properties of fluor-topaz at 1 bar pressure

$\Delta H_{f,298}^\circ$	$= -3084.45 \pm 4.70$ kJ/mol
$\Delta G_{f,298}^\circ$	$= -2910.66 \pm 4.74$ kJ/mol
S_{298}°	$= 105.4 \pm 0.2$ J/(mol·K)
$C_p^\circ = 471.41 - 0.08165T + 1.2695 \times 10^6 T^{-2} - 5485.5 T^{-0.5}$ J/(mol·K)*	

* Valid over the range 200–1000K.

any dissolution experiment will reflect the cumulative composition of that particular batch of solvent. This problem has not been reported for molten-salt calorimetric studies of simple oxide systems and has been argued against on the basis of experiment (Charlu *et al.*, 1978). In this study, the addition of the "unusual" component fluorine apparently has changed the character of the calorimeter solution, possibly through the formation of one or more fluoride complexes and changes of coordination of the cations. Similar excess heats have been found by Stein Julsrud of the University of Chicago (oral communication, 1980) and Westrich and Navrotsky (1981) in experiments on other fluoride-oxysalt systems.

Thermodynamic properties of fluor-topaz

The standard state (298.15 K, 1 bar) thermodynamic properties of fluor-topaz can be derived from the experimental data presented here. In order to derive the entropy, the measured data were extrapolated smoothly to zero from the temperature interval 10–16 K. Over the range from 0–10 K, values for enthalpy and entropy were obtained by graphical integration. From 10–380 K, the data were analytically smoothed by using cubic spline functions. The contributions to $S_{298}^\circ - S_0^\circ$ caused by the extrapolation of the measurements below 10 K is 0.018 J/mol·K. Smoothed values for C_p°, $S_T^\circ - S_0^\circ$ $(H_T^\circ - H_0^\circ)/T$, and $(G_T^\circ - H_0^\circ)/T$ are listed in Table 4.

For ideal fluor-topaz, there should be no zero-point entropy because all the aluminum sites are octahedral, excess alumina (substituting for Si) is not observed in natural topazes (Ribbe and Rosenberg, 1971), and all the (F,OH) sites are filled by fluorine.

A four-term polynomial was fit to the adiabatic (200–380 K) and differential scanning heat capacity measurements, using PHAS20 (Haas and Fisher, 1976). The standard deviation of the fit to these data

These possible errors should be small and have been neglected. Even if one or more of these errors were important, it would not change the observation of the excess heat of solution, although it would change the absolute values of the heats of solution. The observed difference shows an excess heat of solution in $Pb_2B_2O_5$ melts for $CaO-Al_2SiO_4F_2$ mixtures. Consequently, the heat effect observed for

is 0.7 percent. This equation is considered to be accurate to within 1.4 percent to 1,000 K. Above 1,050 K $(dC_p/dT) < 0$ so this equation should not be used for extrapolation to higher temperatures. The thermodynamic properties at 298.15 K (Table 5) were derived given the heat of reaction (1), the ancillary data for the other phases (taken from Robie *et al.*, 1979), and the entropy and heat capacities obtained here. The uncertainty in the enthalpy and Gibbs free energy arises mostly from the uncertainty in the heat of solution of the CaO + $Al_2SiO_4F_2$ mixture.

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