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Crystalline Beryllium Hydride

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Crystalline BeH₂ was prepared by high-pressure compaction-fusion of amorphous BeH₂ catalyzed by 0.5–2.5 mol % lithium. Pressures of at least 2.75 kbar (at 200 °C) as well as temperatures exceeding 130 °C (at 6.2 kbar) were required for the transformation. This was accompanied by an increase in density from 0.62–0.65 g/cm³ for amorphous BeH₂ to 0.77–0.78 g/cm³. Two separate crystalline phases were identified. X-ray diffraction patterns of the low-temperature phase were indexed for a hexagonal unit cell with dimensions $a = 4.20 \text{ \AA}$ and $c = 6.76 \text{ \AA}$ with a theoretical density of 0.82 g/cm³.

Introduction

All preparations of beryllium hydride reported to date give amorphous, polymeric solids containing hydrogen-bridged BeH₂Be groups.^{1–3} The insolubility and nonvolatile character of BeH₂ is consistent with long chains having many repeating monomer units. Unlike the related covalent hydrides MgH₂⁴ and AlH₃,⁵ no crystalline form of nonsolvated BeH₂ has been reported. Holley and co-workers⁶ obtained X-ray diffraction patterns for BeH₂ etherates containing about 60 wt % BeH₂. X-ray powder patterns have been published for BeH₂·0.21Et₂O,⁷ but there is no evidence that any of these data represent the (BeH₂)_n structure itself.

We report the production and characterization of nonsolvated crystalline BeH₂ by the compaction-fusion of amorphous BeH₂, catalyzed by 0.5–2.5 mol % lithium.

Experimental Section

All experiments were conducted under a moisture-free nitrogen atmosphere. Owing to the pyrophoric nature of beryllium alkyls and the toxicity of the products, a glovebox was employed in transferring reactants to the pyrolysis and compaction apparatus.⁸ Solvents were dried by conventional methods.

Equipment. Compaction-fusion of BeH₂ was carried out using (1) piston-mold and (2) hydrostatic equipment. Piston-molds were cylinders, 1.27-cm i.d. × 6.35-cm o.d. × 7.62-cm length, fitted with close-tolerance, polished plungers. They were constructed from case-hardened ASTM 440C steel, enclosed by a 1500-W electrical heater and metal bellows through which dry nitrogen could be circulated. Cooling was provided by pumping water through tubing coiled around the mold. Pressure was supplied by a 50-ton hydraulic (platen) press. Temperature was measured by a thermocouple inserted in a well, drilled axially halfway down the piston.

The hydrostatic compaction-fusion equipment consisted of a Harwood Engineering Co. 13.8 kbar pneumatically operated pressure-generating unit and pressure vessels. One of the vessels was 15.24-cm o.d. × 2.54-cm i.d. × 26.67-cm length; the other was 40.64 cm o.d. × 5.08-cm i.d. × 50.8-cm length. Both were rated at 13.8 kbar. Pressure was measured using a bulk modulus cell with a pneumatic transmitter and receiver-recorder. The pressure vessels were heated electrically and cooled by circulating water through coils wound around them. Temperatures were measured by thermocouples attached to the surface and also positioned in the plug closure at the end of each vessel. The hydraulic fluid consisted of a mixture of white gasoline containing 15 vol % Esso Univas P48 oil, which will not solidify

at pressures well above 6.9 kbar. The pressure vessels were operated behind a barricade made of 1.27-cm steel plate.

Analytical Measurements. X-ray powder data were obtained with a Philips Norelco X-ray unit, using a 114.6 mm diameter camera with Ni-filtered Cu K α radiation. Intensities were estimated visually. Densities were measured by a sink-float technique, employing benzene, *n*-nonane, mesitylene, and methylcyclohexane at varying temperatures. The density of the sample was obtained from the solvent temperature-density relationship at the point of sink-float equilibrium. Methods for determination of hydride hydrogen, beryllium alkyls and alkoxides, and chloride are described in a preceding paper.³ Analysis for lithium was carried out by flame photometry of the acid hydrolysate.

Preparation of Lithium-Doped BeH₂. Lithium was introduced into amorphous BeH₂ in two different ways: (a) by mechanical mixing of the solids, preferably by grinding them together, and (b) by adding an alkyllithium compound to the (*t*-Bu)₂Be-Et₂O prior to solution pyrolysis. In a typical pyrolysis experiment, 0.41 g (6.3 mmol) of *n*-butyllithium (as a 22% solution in hexane) was mixed with 50 g (253 mmol) of (*t*-Bu)₂Be-Et₂O and the mixture added to well-stirred dodecane as quickly as possible while maintaining a temperature of 200 ± 5 °C. After 10 minutes, the resulting slurry was cooled quickly and filtered, and the solids were washed with 200 mL of petroleum ether and dried for 1 h in vacuo at 100 °C. The BeH₂ product (94.1 wt % purity) was a white-to-gray powder ($d = 0.66 \text{ g/cm}^3$), which reacted slowly with moist air or water.

Crystallization of BeH₂ by Compaction-Fusion. A. With the Piston-Mold Unit. A retainer plug was placed in the bottom of the mold and the Li-doped BeH₂ powder added in several increments, tamping down well after each addition, until 0.4–0.5 g was charged. The piston and bellows assembly were fitted in place and positioned between the platens of the hydraulic press. The predetermined pressure was applied and the mold heated to the desired temperature, while the pressure was held constant. After the pressure and temperature were maintained for a set time, the mold was cooled either slowly or quickly, by circulating water through the cooling coil. When the temperature reached about 60 °C, pressure was released, the unit disassembled, and the BeH₂ pellet pressed into a nitrogen-flushed container. It was then broken up or pulverized for density determination and analysis.

B. Using Hydrostatic Compaction. A 1.9-cm o.d. × 0.051-cm wall × 10.2-cm flat-bottom seamless aluminum capsule was placed in a close-fitting, tapered split mold and 3–4 g of the Li-doped BeH₂ powder introduced and precompacted with a piston at 1.4 kbar. This was done in several increments to obtain efficient capsule loading. (Capsules employed with the large pressure vessel were 4.45-cm o.d.

Table I. X-ray Powder Diffraction Data for Crystalline BeH₂

low-temp phase 338-208				high-temp phase 378-295			
<i>d</i> , Å	<i>I</i> / <i>I</i> ₀	<i>d</i> , Å	<i>I</i> / <i>I</i> ₀	<i>d</i> , Å	<i>I</i> / <i>I</i> ₀	<i>d</i> , Å	<i>I</i> / <i>I</i> ₀
3.38	s	2.08	s	3.78	s	1.67	vw
3.22	vw	1.96	vw	2.95	s	1.35	vw
2.94	vw	1.78	w	2.86	m	1.26	vw
2.84	vw	1.35	w	2.07	m	1.19	vw
2.69	vw			1.94	vw	1.14	vw
				1.84	vw	1.09	vw
				1.72	vw		

× 0.064-cm wall × 15.2-cm length and held about 55 g of feed.) The capsule was then sealed with a close-fitting stainless steel plug fitted with two Viton O-rings and placed in the cavity of the pressure vessel. The desired hydrostatic pressure was applied and the vessel heated to the predetermined temperature while the pressure was held constant. At the end of the desired hold period the vessel was cooled to about 60 °C before pressure was released. The compacted BeH₂ was recovered in the form of a very hard, gray cylinder by tearing open the capsule. It was broken up with a small ceramic jaw crusher and pulverized prior to analysis.

Alternative means of encapsulating the amorphous Li-doped BeH₂ for hydrostatic compaction involved precompaction in piston-mold equipment. This was done by applying 1.4-kbar pressure and then releasing the pressure and heating the mold to 160–180 °C. A glassy, amorphous form of BeH₂ was produced, with an increase in bulk density from 0.10–0.15 to 0.62–0.65 g/cm³. The resulting pellet was encapsulated in aluminum or tin foil or sealed in heat-shrinkable Teflon tubing for compaction–fusion.

Results and Discussion

Crystalline Phases. High-pressure compaction–fusion of amorphous BeH₂ gave two different polymorphs, depending upon crystallization temperature and pressure. In this paper the high-temperature form is designated phase 378-295 and the low-temperature form phase 338-208 (from the two strongest lines in the X-ray diffraction patterns, shown in Table I). Each polymorph had properties of a hard, vitreous-like solid. Crystallite size was very small; in no preparation was there any visible evidence of crystallinity. Since this prevented single-crystal work, Debye–Scherrer powder patterns for phase 338-208 were indexed on the basis of a hexagonal unit cell of dimensions *a* = 4.20 Å and *c* = 6.76 Å. Selected area electron diffraction patterns confirmed the hexagonal system and indicated there are four molecules per unit cell with a calculated density of 0.82 g/cm³. The crystal habit of phase 378-295 was not conclusively identified, although the data fit either the monoclinic or tetragonal system reasonably well.

Effect of Lithium Concentration. High-purity, amorphous BeH₂ probably can be crystallized at ultrahigh pressure and elevated temperature; however, it is readily accomplished by first introducing a small amount of lithium into the feed. One method consists simply of mixing LiH, LiAlH₄, Li₂BeH₄, etc. with the amorphous powder prior to compaction–fusion. A more effective way is to add the desired amount of an alkyl lithium compound, e.g., *n*-butyllithium, to (*t*-Bu)₂Be–Et₂O before pyrolysis to BeH₂.³ This produces a much more intimate mixture of LiH with BeH₂ and requires less time for completion of crystallization, compared with that for the physically mixed feed. Table II shows the effect of lithium concentration on the degree of crystallization. As little as 0.5 mol % LiH is needed to give a positive effect, although almost 2.5 mol % should be added to produce maximum density. However, as more LiH is introduced, the product becomes more moisture-sensitive. A small decrease in BeH₂ purity usually occurs during compaction–fusion as the result of thermal decomposition, producing free Be metal.

The mechanism by which LiH induces crystallization is not clearly understood. It possibly acts as a seed to initiate crystal lattice formation in the pseudo-melt. BeH₂ is not believed actually to melt under these conditions, though it can be

Table II. Effect of Lithium Concentration on Crystallization of BeH₂^a

mol % Li ^b	BeH ₂ purity, % ^c		product density, g/cm ³ ^d		X-ray data	
	before crystn	after crystn	before crystn	after crystn	338-208	378-295
0.25	95.1		0.68	0.70	vw	vw
0.5	93.8		0.67	0.72	w	w
1.0	96.2	95.8	0.67	0.75	s	s
2.5	94.1	91.2	0.68	0.78	vs	s
5.0	95.3	86.8	0.69	0.78	vs	s
10.0	93.7	93.1	0.67	0.77	vs	s

^a Compaction–fusion conditions (13.8 kbar at 200 °C for 70 min) in piston-mold. ^b Added as *n*-BuLi to (*t*-Bu)₂Be–Et₂O before pyrolysis. ^c Hydride contributed by LiH included. ^d By sink–float method.

Table III. Effect of Applied Pressure–Temperature on BeH₂ Crystalline Phase Distribution^{a, b}

<i>P</i> , kbar ^c	<i>T</i> , °C				
	150	175	200	225	250
6.9	30/0	<100/0	97/3	97/0	100/0
10.3	95/5	95/0	97/3	95/5	62/38
13.8	95/5	100/0	90/10	50/50	45/55
17.2	70/5	95/5	70/30	20/80	2/98
20.7	<90/<10	63/37	60/40	23/77	5/95

^a Estimated distribution in % phase 338-208/% phase 378-295; figures that do not total 100% represent incomplete crystallization; the remainder denotes amorphous material. ^b Feed composition (wt %): BeH₂, 95.2; Li, 1.3; BeR₂, 1.7; Be(OR)₂, 0.15; Cl, 0.35. ^c By piston-mold.

extruded from a die. More likely, the LiH serves to terminate the BeH₂ polymer chains, effectively shortening them for subsequent reorientation under pressure. It is noteworthy that as little as 0.5–1 Li atom for each 100 Be atoms can effect crystallization. Comparison of the X-ray powder patterns of 2.5 mol % Li-doped crystalline BeH₂ with that of Li₂BeH₄⁹ does not indicate formation of the latter as a discrete compound.

Temperature–Pressure Effects. The effect of variations in temperature and applied pressure on crystalline phase distribution over the range 150–250 °C and 6.9–20.7 kbars is shown in Table III. The piston-mold equipment used to obtain these data experienced some problems in accurately reproducing pressure, which can explain discrepancies in phase distribution. Nevertheless, the data clearly show that crystallization to phase 338-208 begins at conditions just below 150 °C and 6.9 kbar and that phase 378-295 predominates at higher temperature and pressure.

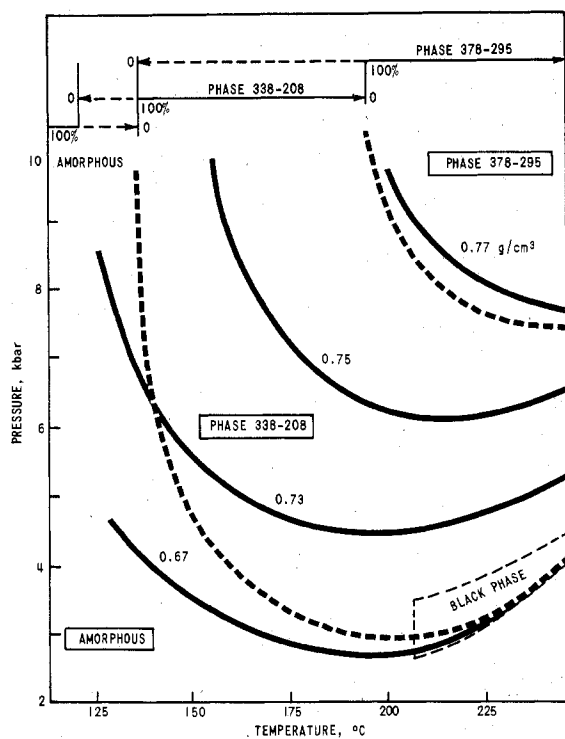
Table IV gives a comparison of crystalline phase distribution obtained with piston-mold and hydrostatic compaction equipment, employing the same feed (95.2 wt % BeH₂, 1.3 wt % Li). The data show that much higher indicated pressures must be applied by the piston-mold to obtain equivalent hydrostatic compaction results. The difference is believed due to frictional pressure losses between the piston and wall caused by extrusion of abrasive BeH₂. Very short treatment times are undesirable, but even very long hold times do not narrow the differences between the two techniques.

A good phase diagram for BeH₂ was not defined in this study. The data did enable us to generate a *P*–*T* diagram (Figure 1) delineating approximate phase stability regions and isodensity lines, encompassing the ranges 2.75–9.7 kbar and 120–245 °C. Only hydrostatic compaction data were used. Compaction time was not a critical variable, as densification was essentially complete in 1 h. However, at crystallization threshold conditions, times up to 4 h were used. A pressure of at least 2.75 kbar (at about 200 °C) and a temperature of

Table IV. Comparison of Piston-Mold with Hydrostatic Compaction of BeH_2^a

compaction method	test conditions ^b		phase distribution, % ^c		
	P, kbar	time, min	amor-phous	phase 338-208	phase 378-295
piston-mold	6.9	30	100	0	0
	6.9	120	0	95	5
	6.9	240	0	99	1
	10.3	5	45	50	5
	10.3	30	0	95	5
	13.8	<0.5	100	0	0
	13.8	1	0	95	5
	13.8	15	0	90	10
	13.8	60	0	90	10
hydrostatic	2.75	240	0	95	5
	4.1	60	0	99	1
	4.1	240	0	95	5
	5.9	60	0	90	10
	5.9	240	0	75	25
	6.9	30	0	20	80
	6.9	120	0	20	80
	6.9	240	0	20	80

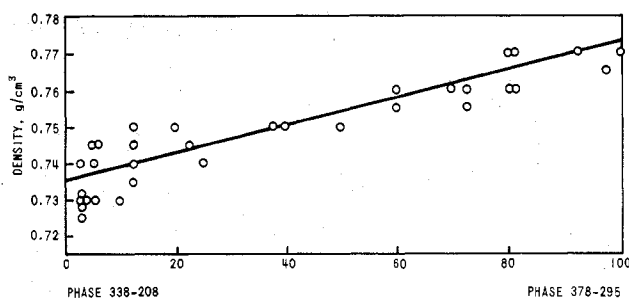
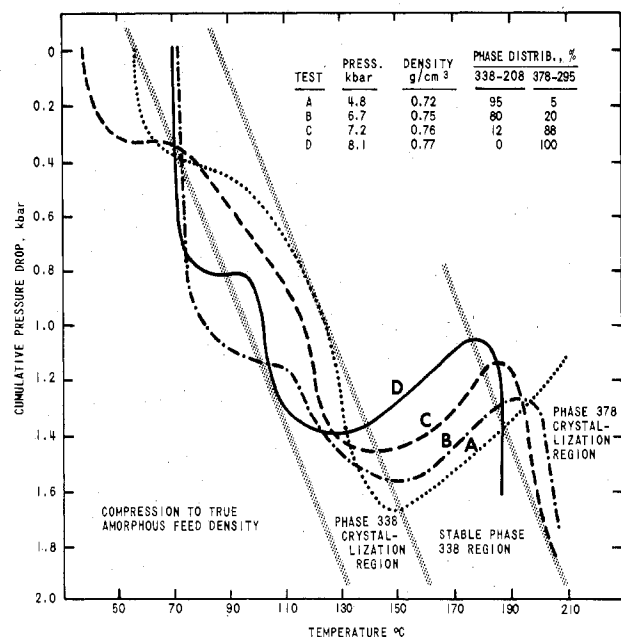
^a Feed composition (wt %): BeH_2 , 95.2; Li, 1.3; BeR_2 , 1.7; Be(OR)_2 , 0.15; Cl, 0.35. ^b At temperatures of 200–205 °C. ^c Visually estimated.

**Figure 1.** Pressure-temperature diagram for BeH_2 polymorphs.

at least 130 °C (at pressures above 6.2 kbar) appear to be required for crystallization of BeH_2 .

The relationship between BeH_2 crystalline phase distribution and density is shown in Figure 2. The densities 0.73–0.78 g/cm^3 are below the theoretical value of 0.82 g/cm^3 and can largely be explained by the presence of small internal cavities formed by H_2 released during trace decomposition of BeH_2 , as well as some residual amorphous material in phase 338-208.

Low-temperature phase 338-208 could be converted to phase 378-295 by applying the necessary temperature and pressure, but the opposite transformation was never achieved without inversion first to the amorphous form. Phase 378-295 actually was quite stable; it survived heating at 175 °C for over 5 days. When a 1:1 mixture of phases 338-208 and 378-295 was

**Figure 2.** Crystalline BeH_2 : Variation of density with composition.**Figure 3.** BeH_2 crystallization: Effect of hydrostatic pressure drop with temperature.

heated to 175 °C for 2 days at atmospheric pressure, all X-ray diffraction lines for phase 338-208 disappeared. Then, when the sample was resubjected to compaction-fusion, the two phases were recovered at their original concentration.

Insight into the densification process was provided by tests made with the larger pressure vessel (5.08 cm \times 50.8 cm cavity). Because of higher feed loadings, density changes during compression could be recognized by a pressure drop in the system. The relationship between pressure drop and temperature during the heating period is shown in Figure 3. There was a sharp initial pressure drop at the beginning of a run due to compaction of the amorphous feed (bulk density about 0.32 g/cm^3) to its true density of about 0.67 g/cm^3 . The second pressure drop occurred in the range 100–140 °C, which represents crystallization to phase 338-208 ($d = 0.73$ – 0.74 g/cm^3). Thereafter, a steady increase in pressure was observed, due to thermal expansion of the hydraulic fluid. The transition to crystalline phase 378-295 ($d = 0.77$ – 0.78 g/cm^3) finally took place at a temperature of 180–200 °C. It should be noted that test A, made at 4.8 kbar, did not give this third pressure drop; and only a trace of phase 378-295 was obtained.

A curious form of BeH_2 was discovered during this study of crystallization variables. Normally, the compacted Li-doped BeH_2 was white to light gray in color. However, in several instances tests conducted in the relatively narrow regime of 2.75–3.8 kbar at 205 °C to 4.1–4.5 kbar at 245 °C gave a glassy, black product ($d = 0.67$ – 0.68 g/cm^3). Chemical, IR, and X-ray diffraction analyses showed it to be indistinguishable from the normal, compacted material. Surprisingly, there was no increase in free Be metal which could have accounted for

the color. This material was not characterized further, but its density and conditions of preparation place it at the transition region between fused, amorphous BeH_2 and phase 338-208. It may represent a transitory structure in which electrons are largely delocalized and free to migrate within the incipient lattice (similar to F centers).

Crystallization of BeH_2 Slurry. An alternative procedure to hydrostatic compaction of encapsulated dry feed utilized the slurry of BeH_2 directly as it was recovered from the solution pyrolysis reaction.³ The same types of aluminum capsules employed with the dry-feed procedure were used, these being filled with a slurry of the amorphous Li-doped BeH_2 in the pyrolysis medium. Best results were obtained at solid concentrations of 20–70% and pressures of 5.5–9.7 kbars at 205–230 °C. Phase 338-208 predominated in all crystallized slurry products except at the most rigorous conditions—9.7 kbar and 230 °C, where phase 378-295 was produced in 55% concentration.

Other Additives. A number of additives to amorphous BeH_2 other than lithium were tested, but none proved as effective in promoting crystallization. These included various complex metal hydrides containing Be, B, and Al, AlH_3 and alkyl-aluminum compounds, and others. Coadditives to the Li-doped BeH_2 also were tested. The alkali and alkaline earth fluorides as well as Be powder showed some effect in lowering the crystallization pressure and time requirements. Similarly, a 1:1 mixture of crystalline and amorphous BeH_2 could be densified using 13.8-kbar pressure alone. However, this effect was not sustained through more than one or two cycles. The

density of the product dropped regularly as the concentration of original seed decreased.

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Registry No. BeH_2 , 7787-52-2.

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Preparation and Characterization of Some Monofluoroselenite and -tellurite Compounds

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Compounds with the related anions monofluoroselenite and tellurite, SeO_2F^- and TeO_2F^- , have been prepared and characterized. $\text{M}^1(\text{SeO}_2\text{F})$ ($\text{M}^1 = \text{Cs}, \text{Me}_4\text{N}, \text{Et}_4\text{N}$) compounds are readily prepared from aqueous solutions. The vibrational spectrum of the SeO_2F^- ion has been firmly established by IR and Raman spectroscopy on the solids and polarization measurements on solutions of $\text{Et}_4\text{NSeO}_2\text{F}$ in acetonitrile. CsSeO_2F has been shown to be isomorphous with CsBrO_3 . Three monofluorotellurite compounds, $\text{M}^1(\text{TeO}_2\text{F})$ ($\text{M}^1 = \text{Na}, \text{K}, \text{Me}_4\text{N}$), have been prepared and characterized. Melts of TeO_2 with NaF and KF yield the monofluorotellurite compounds and not mixtures of M^1F and $\text{M}^1_2\text{TeO}_2\text{F}_2$ as found for $\text{M}^1 = \text{Cs}$ and Rb . The vibrational spectra have been reported.

Introduction

Selenium and tellurium in oxidation state IV form both difluoro^{1,2} and pentafluoro³ anions $\text{MO}_2\text{F}_2^{2-}$ and MF_5^- . Selenium forms in addition the monofluoro^{2,4} and trifluoro anions⁵ SeO_2F^- and SeOF_3^- , while tellurium gives a tetrafluoroanion¹ TeOF_4^{2-} . Recently, NMR evidence has been presented for the existence, in acetonitrile solution, of the TeF_6^{2-} ion,⁶ a species sought by several research groups.^{1,7} The monofluorotellurite anion is unknown. Milne and Moffett¹ attempted to prepare the rubidium and cesium monofluorotellurites from 1:1 melts of the alkali metal fluoride and tellurium dioxide. The product was found to be a mixture of $\text{M}^1_2\text{TeO}_2\text{F}_2$ and TeO_2 . It was considered of interest to attempt to prepare $\text{M}^1\text{TeO}_2\text{F}$ compounds using other ionic fluorides and different methods.

Although monofluoroselenites are well-known,^{2,4} it is not clear whether they exist as individual or as condensed anions in the solid state. The present study of the SeO_2F^- ion was undertaken to clarify this question.

Experimental Section

Materials. Selenious acid (Merck) was used directly; selenium dioxide (Ventron) was pumped dry at ca. 70 °C for several hours; tellurium dioxide (Fisher) was used directly. Potassium (BDH) and cesium (Fluka) fluorides were dried at 650 °C under a stream of N_2/HF before use. Sodium fluoride (Ventron ultrapure) was used directly. Tetraethyl- (BDH) and tetramethylammonium (Merck) hydroxides, 25% aqueous, and 48% aqueous hydrofluoric acid (J. T. Baker) were standardized before use. Acetonitrile (Fisher) was first refluxed over P_2O_5 and then distilled and stored over molecular sieves. Dimethyl sulfoxide (Fisher) was distilled from CaO at reduced pressure and stored over molecular sieves.