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CVD OF BaF₂ WITH NEW STABLE AND VOLATILE COMPLEXES OF BARIUM(II)

D.G. Gilliland*, M.L. Hitchman*, S.C. Thompson** and D.J. Cole-Hamilton**

*Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland

**Chemistry Department, University of St. Andrews, Fife KY16 9ST, Scotland

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Abstract

The new β -diketone, 1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluorononane-4,6-dione (HTDFND) has been prepared and employed in the formation of a complex of Ba. A complex of the same metal derived from the β -diketone, 1,1,1,2,2,3,3,7,7,7-decafluoroheptane-2,4-dione (HDFHD) has also been prepared. The compounds have the formula [M(TDFND)₂H₂O] or [M(DHFD)₂H₂O]. The complexes have been characterised by analytical and spectroscopic means. Simultaneous thermal analysis at one atmosphere reveals that the compounds lose water but then sublime, and in the case of [Ba(TDFND)₂H₂O] without any decomposition. [Ba(TDFND)₂H₂O] is the first barium complex for which this is the case and it can be dehydrated to give [Ba(TDFND)₂] which is also volatile. This suggests that [Ba(TDFND)₂H₂O] could be a suitable precursor for the CVD growth of BaF₂. This has been investigated. On silicon substrates complete orientation in the (111) direction is observed. Changes in the film growth rate with time are attributed to slow reorganisation of the crystal structure of [Ba(TDFND)₂].

Introduction

Laying down thin films of barium containing compounds using the gas phase decomposition of volatile complexes is important for high T_c superconducting films or for coatings of, for example, BaF₂. Several reports have appeared of superconductor growth /1/, but problems arise concerning the reproducibility of growth and the control of the stoichiometry. These problems can often be traced back to inadequacies of the precursors, particularly those of barium /2/. The most commonly used barium precursors are hydrates of β -diketonates (Fig. 1.) with R = R' = ^tBu (DPM), R = R' = CF₃ (HFAC) or R = ^tBu, R' = C₃F₇ (HFOD). All of these compounds are oligomeric and of low volatility so that they decompose at temperatures close to their sublimation temperature. This means that (a) reproducibility of the barium content in the gas phase is poor and (b) a new sample of precursor is required for each growth run.

Two methods have so far been proposed to overcome this problem. The first method involves complexing [Ba(HFA)₂] with a polyether (tetraglyme or hexaglyme) or crown ether to reduce its oligomerisation and increase its volatility /3-5/. However, although the compounds can be sublimed at low pressure, at one atmosphere decomposition occurs at a temperature near

to the sublimation temperature /6/. The second method is to transport the β -diketonate using a carrier gas saturated with amine vapour /7/. In this case complete volatilisation occurs at temperatures well below those found in the absence of the amine.

An alternative approach is suggested from an analysis of published /8/ thermal analytical data for barium β -diketonates which indicates that the % weight left behind after sublimation (which can be regarded as a measure of the stability of the compound during sublimation) decreases in the series $R' = CF_3 > C_2F_5 > C_3F_7$ ($R = tBu$ in each case). This suggests that C_3F_7 may play a special role in reducing the degree of polymerisation of the Ba precursor or in reducing the strength of intermonomer interactions within the polymer. However, even for $R = tBu$, $R' = C_3F_7$ (HFOD), 100% weight loss is not observed showing that some decomposition occurs during sublimation. We have, therefore, increased even further the fluorine containing substituents on the ligand rings and have synthesised the β -diketonates with $R = CF_3$, $R' = C_3F_7$ (DFHD) and $R = R' = C_3F_7$ (TDNFD); a patent application has been filed /9/. These complexes have the general stoichiometry $[Ba(\beta\text{-diket})_2 \cdot H_2O]$ and we report preliminary results for the CVD of BaF_2 with the TDFND complex.

Experimental

Full details of the synthesis of the barium complexes and their characterisation by microanalysis and spectroscopic analysis are given elsewhere /10/ but are summarised in Tables 1 and 2. Thermal analyses were carried out with a Stanton Redcroft thermal analyser at atmospheric pressure under nitrogen and at a heating rate of $20^\circ C \text{ min}^{-1}$. The CVD system was an impinging jet reactor (Archer Technicoat Ltd) with a resistive heated substrate platform (U.S. Inc) and standard gas handling facilities. The stainless steel precursor container was heated by circulating hot air in a separate temperature controlled enclosure. Vapour generated in the container was then carried by a flow of argon gas through a stainless steel gas line. The gas line was fitted with valves which allowed the precursor to be vented to exhaust, permitting stabilisation of the precursor flow before the start of deposition, or to have direct entry to the reactor. All components of the system between the precursor container and exhaust were heated to a temperature of about $20^\circ C$ above the sublimation temperature of the precursor to prevent premature condensation. The precursor was mixed with O_2 oxidant immediately prior to impinging on the heated substrate so minimising the possibility of reaction in the gas phase. Waste gases were passed through a cold trap to condense any unreacted precursor and were then removed from the system by a rotary vacuum pump. The precursor container temperature used was either at $170^\circ C$ or $180^\circ C$ corresponding to a precursor temperature of $160^\circ C$ or $170^\circ C$ respectively. Film deposition was typically undertaken at a heater platform temperature of $700\text{-}750^\circ C$, corresponding to a substrate temperature $\sim 630\text{-}680^\circ C$, a system pressure of 10 Torr, an argon precursor carrier gas flow of 200 sccm and an oxygen flow of 400 sccm. Single crystal materials used as substrates were Si(100) or (111), for XRD measurements and sapphire for film thickness measurements.

The surface morphology of the films was examined using scanning electron microscopy and the chemical composition with energy dispersive analysis of X-rays (JEOL JSM-840A/TRACOR NORTHERN EDAX). Identification of crystalline phases and preferred orientation in the films was achieved using an X-ray powder diffractometer with Cu K-alpha radiation. Film thickness profiles were measured by a surface profilometer (SLOAN DEKTAK II) after films had been photolithographically patterned and etched with a suitable mineral acid.

Measurements of the quantity of precursor transported into the reactor were made by condensing the precursor vapour in a cooled small glass u-tube (weight ~ 20 g) attached to the end of this gas line at its entry point to the reactor. The u-tube was cooled with a mixture of dry ice and trichlorethylene (-60°C). The amount of materials transported (~ 0.5 to 100 mg in 60 min) was monitored as a function of the time the precursor was held at the vaporisation temperature.

Results and Discussion

(i) Thermal Analysis

Data obtained from combined Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) for the new complexes of barium will be reported separately /10/, but a summary is collected in Table 3, together with the data for the known compounds [Ba(HFOD)₂H₂O] and [Ba(DPM)₂H₂O] for comparison. A comparison of STA traces for [Ba(HFOD)₂H₂O], [Ba(DFHD)₂H₂O], [Ba(TDFND)₂H₂O] and [Ba(TDFND)₂] is shown in Figure 2a-2d. For all the molecules there are features near 100°C (peak (i) in all cases and peaks (i) and (ii) in 2a) corresponding to loss of water, and sharp melting points (iii) are observed ~ 200°C. Of more importance for CVD applications, however, is the sublimation (iv) and decomposition (v) behaviour. It is noteworthy that in changing from ^tBu to CF₃ to C₃F₇(HFOD → DFHD → TDFND) there is a decrease in the onset of sublimation (Table 3 and Figure 2) but that the onset of decomposition occurs at higher temperatures. Thus, for [Ba(HFOD)₂H₂O] decomposition occurs about halfway through the sublimation so that only ca 60% of the complex sublimates under these conditions. For [Ba(DFHD)₂H₂O] the onset of decomposition occurs just at the high temperature end of the sublimation feature so that ca 65% of the complex sublimates under these conditions. For [Ba(TDFND)₂H₂O], however, there is no sign of decomposition and 100% weight loss is observed indicating that the complex sublimates completely under these conditions. This is the first barium complex to be shown to sublime completely without decomposition at one atmosphere. Presumably the enhanced volatility and stability arise from reduced intermonomer forces within the polymeric structure of the complex.

As shown in Table 3 the new compounds readily lose water on heating under one atmosphere of nitrogen. Since this may have an effect on the reproducibility of transport of the precursor, we have examined, as an example, the dehydration of [Ba(TDFND)₂H₂O]. Dehydration was carried out either in situ in the thermal analyser by heating the sample to 180°C for 0.5h, cooling and re-running the STA, or by heating a bulk sample of the solid at 100°C in vacuo. Using either technique, microanalysis, i.r., ¹H n.m.r., ¹⁹F n.m.r., and STA all showed that the compound was water free [Ba(TDFND)₂] (see Tables 1, 2 and 3 respectively). In particular, thermal analysis of this compound showed features very similar to those of [Ba(TDFND)₂H₂O] except that the endotherm corresponding to water loss ((i) in Figure 2c) was absent (see Figure 2d). On closer examination, however, it is clear that certain other changes have occurred. The melting is similar but the onset of the major sublimation ((iii) in Figure 2c and d) occurs at a higher temperature. From these results one might expect to see a variation with time in the sublimation rate of the precursor and the growth rate of BaF₂ from the TDFND complex of barium. This is examined in the next two Sections.

(ii) Sublimation Rates

Figure 3 shows the variation of sublimation rate with the length of time the precursor sample of the TDFND complex of barium is held at the vaporisation temperature of 170°C.

For the first few runs there is no decrease in sublimation rate with time, which is a little unexpected from the results above for loss of water from the sample, and there is in fact a small increase; this effect is being investigated further to see if it is reproducible. However, after about 10 hours a decrease does set in and the loss of volatility anticipated is evident. Deposition of BaF_2 from the TDFND complex of barium shows a similar fall off in growth rate with time, as discussed in the next Section.

(iii) CVD

Figure 4 shows a typical diffractogram of a BaF_2 film grown on Si from $[\text{Ba}(\text{TDFND})_2\text{H}_2\text{O}]$. The films were strongly adherent to the substrates and, as Fig. 4 shows, were completely orientated with the (111) direction orthogonal to the substrate surface; the lines of the (111) family out to (333) are readily apparent. BaF_2 has also been reported to be formed on decomposition of $[\text{Ba}(\text{HFA})_2\text{H}_2\text{O}]$ /13/ or $[\text{Ba}(\text{HFOD})_2\text{H}_2\text{O}]$ /12/ and partial or full orientation is observed.

Figure 5(a) shows variations of layer thickness with radial distance for a number of growth runs using the same sample of precursor, carried out under identical conditions over a period of two days. The bell shaped curves are characteristic of transport controlled growth for an impinging jet reactor /14/. The initial growth rate of BaF_2 from $[\text{Ba}(\text{TDFND})_2\text{H}_2\text{O}]$ is very high ($\sim 0.8 \mu\text{h}^{-1}$) and about three times higher than that observed using $[\text{Ba}(\text{HFOD})_2\text{H}_2\text{O}]$ under similar conditions (cf Figure 5(b)). However, Figure 5(a) shows a marked drop in growth rate over the two day period. Visual examination of the precursor material recovered after this series of experiments showed a slight discolouration towards brown but i.r., ^1H n.m.r. and ^{19}F n.m.r. spectra were identical to those of $[\text{Ba}(\text{TDFND})_2]$ (see Table 2). A very small amount (< 5%) of an insoluble brown solid was also present. STA studies of the recovered precursor material were again found to be very similar to those of $[\text{Ba}(\text{TDFND})_2]$ (Figure 2d). Interestingly, the melting point (196°C) but not the sublimation temperature is higher than that obtained from freshly prepared $[\text{Ba}(\text{TDFND})_2]$ and this sample does not take up moisture from the air over several days. In contrast, a similar sample examined after being used for only a short period as precursor, had an intermediate melting point (190°C) and became rehydrated to some extent over a two day period, as evidenced by STA studies.

Conclusions

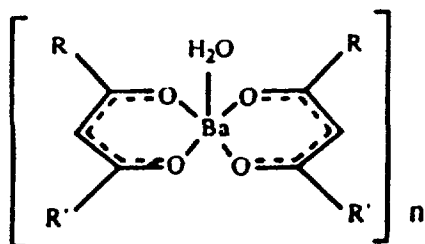
The strategy of increasing the fluorine containing substituents on the ligand rings of β -diketonates of barium has been shown to lead to a progressive increase in the stability of the complexes and a substantial increase in the volatility, despite the large increase in relative molecular mass. In particular, the $[\text{Ba}(\text{TDFND})_2\text{H}_2\text{O}]$ complex with four C_3F_7 groups attached to the rings is found by STA to show 100% volatilisation. However, it is also found that there are small and subtle changes in the melting and sublimation characteristics of the complex on dehydration and prolonged heating. These changes are reflected in decreases in the complex sublimation rate and the growth rate of BaF_2 . The results suggest that the $[\text{Ba}(\text{TDFND})_2]$ formed by dehydration of $[\text{Ba}(\text{TDFND})_2\text{H}_2\text{O}]$ undergoes slow structural changes in the solid and /or melt which lead to stronger inter-monomer forces and decreased volatility. The compound does retain some volatility and the effect is being investigated further to ascertain whether or not a stable level of volatility is reached. However, the slow nature of the rearrangement would be a distinct drawback for its use in the production of, for example, superconducting layers of YBCO where reproducible control of stoichiometry is an essential prerequisite.

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R	R'	abbreviation
Me	Me	ACAC
^t Bu	^t Bu	TMHD
^t Bu	CF ₃	TPM
^t Bu	C ₂ F ₅	PPM
^t Bu	C ₃ F ₇	HFOD
CF ₃	CF ₃	HFAC
CF ₃	C ₃ F ₇	DFHD
C ₂ F ₅	C ₂ F ₅	DFD
C ₃ F ₇	C ₃ F ₇	TDFND

Figure 1 General formula of barium β -diketonates with possible specific substituents. Note that in some cases the number of water molecules may be greater than one and also that anhydrous compounds have been isolated.

Table 1: Microanalytical Data for New Complexes

Complex	Found %		Expected %		Relative Molecular Mass Found (Expected)
	C	H	C	H	
[Ba(DFHD) ₂ (H ₂ O)]	21.7	0.5	21.9	0.5	964 ^a (969)
[Ba(TDFND) ₂ (H ₂ O)]	22.2	0.4	22.3	0.4	
[Ba(TDFND) ₂]	22.6	0.13	22.7	0.21	

^ain methanolTable 2: Selected Spectroscopic Data for β -diketones and their Complexes

Compound	i.r. (max/cm ⁻¹) ^a		¹ H n.m.r.(δ) ^b			¹⁹ F n.m.r. ^b	
	ν (O-H)	ν (C-O)	ν (C-C)	C-H	O-H	CF ₃ ^c	CF ₂ ^d CF ₂ ^e
HDFHD				6.6	12.9		
HTDFND				6.4	12.6		
[Ba(DFHD) ₂ H ₂ O]	3420 br	1655 s	1530 s br	5.85			
[Ba(TDFND) ₂ H ₂ O]	3550 v br	1650 s	1515 s br	5.90		81(t)	120(q) 126.5(s) ^f
[Ba(TDFND) ₂] ^g		1650 s	1505 s br	5.90			
[Ba(TDFND) ₂] ^h		1650 s	1505 s br	5.90			

^aAll DFHD complexes have peaks at λ_{\max} : 1350 m, 1225 s, 1205 sh, 1180 w sh, 1142 s, 1118 m, 1090 sh, 1012 sh, 960 m, 928 m, 797 m, 778 w, 732 m, 718 m, 660 w, 625 w br, 570 m, 520 w br, 460 w. All TDFND complexes have peaks at λ_{\max} : 3140 w, 1340 m, 1280 sh, 1220 s br, 1180 s, 1140 m, 1115 s, 1060 w, 960 m, 920 m, 885 w, 873 m, 852 w, 790 m, 785 sh, 745 m, 727 m, 680 w, 670 w, 630 m, 588 sh, 530 m, 460 m. ^bIn methanol at room temperature, OH protons obscured by solvent, chemical shifts in ppm to high frequency of TMS or CF₃Cl; ^cCF₃ of C₃F₇ group; ^dCF₂ next to CF₃; ^eCF₂ next to metal; ^fpeaks essentially unchanged to -100°C; ^gsample formed by heating [Ba(HFOD)₂H₂O] for 1 h *in vacuo* at 80°C; ^hsample recovered after 10 h of using [Ba(TDFND)₂H₂O] in growth reactor.

Table 3: Thermal Analysis Data for Barium β -diketonate Compounds

Compound	Water loss		Melt T/°C	Sublimation		Decomposition Onset/°C	Total Weight loss/%
	Onset T/°C	Weight loss %		Onset T/°C	Weight loss/% ^a		
[Ba(DPM) ₂ H ₂ O]	50,90	3,7	b	200,320 ^c	30	420,580,700 ^d	84
[Ba(HFOD) ₂ H ₂ O]	20,70	2	176	240	38	300	91
[Ba(DFHD) ₂ H ₂ O]	80	2	200	220	88	350	91.5
[Ba(TDFND) ₂ H ₂ O]	63	2	187	150,200 ^c	98	b	100
[Ba(TDFND) ₂] ^e			186	130,220 ^c	92	b	92
[Ba(TDFND) ₂] ^f			196	130,220 ^c	98	b	98

^aprior to onset of decomposition; ^bnot observed; ^coccurs in two stages; ^dresidue melt(?); ^efreshly prepared (after 0.5 h dehydration at 180°C in the STA); ^faged (after use for > 10 h in growth reactor - recovered sample).

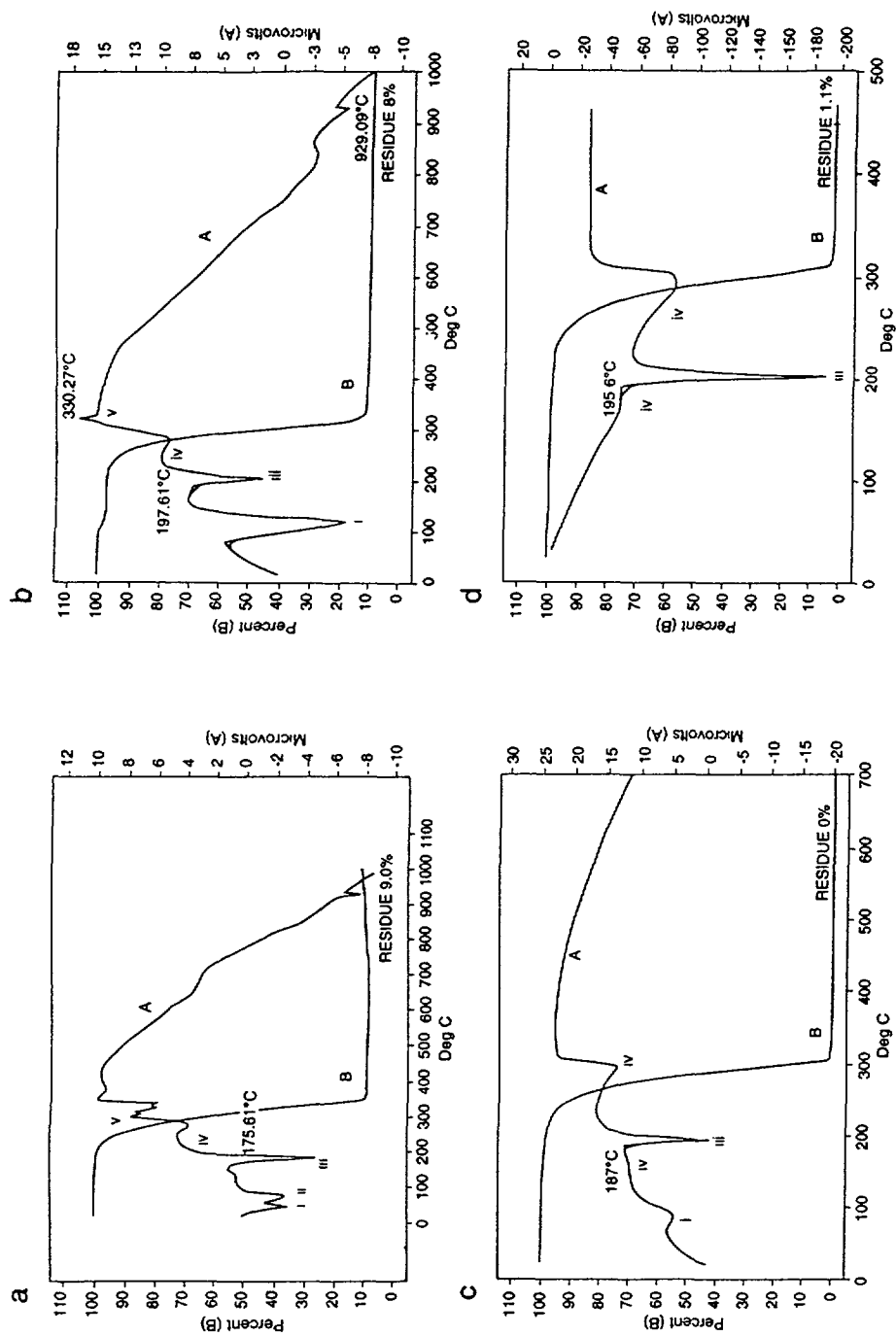


Figure 2 Simultaneous Thermal Analysis traces for barium β -diketonate complexes under nitrogen.
 (a) [Ba(HFOD)₂H₂O]; (b) [Ba(DHFD)₂H₂O]; (c) [Ba(TDFND)₂H₂O]; (d) [Ba(TDFND)₂] recovered after 10 hours use as a precursor for growth of BaF₂.

Key: Curves A: DTA B: TGA (weight loss)

Peaks: (i) and (ii) loss of water; (iii) melt; (iv) sublimation; (v) decomposition.

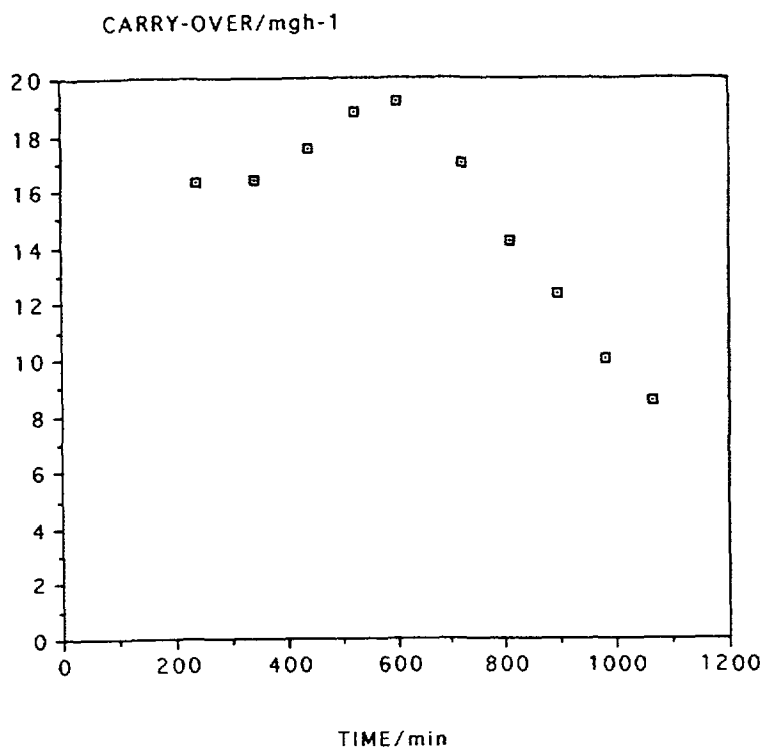


Figure 3 Sublimation rates for $[\text{Ba}(\text{TDFND})_2\text{H}_2\text{O}]$ as a function of vapourisation time. Sublimation temperature 170°C .

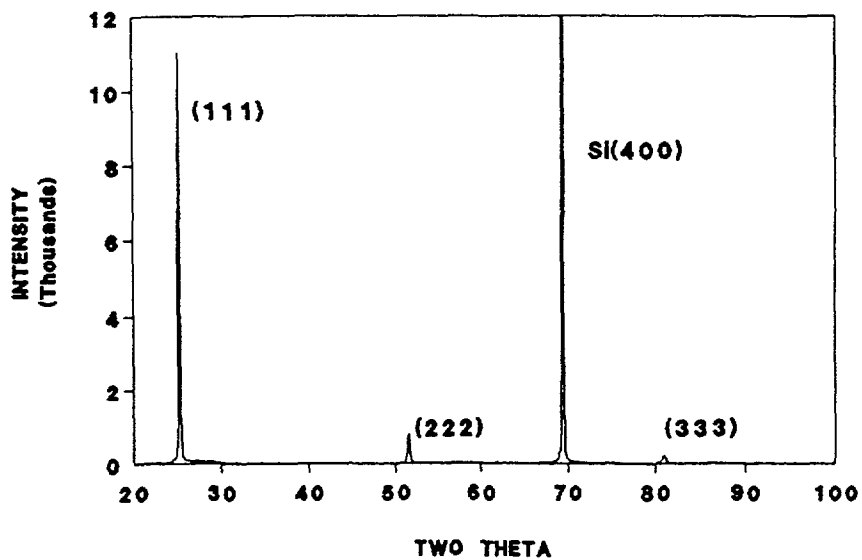


Figure 4 X-ray diffractogram for BaF_2 deposited at 730°C on $\text{Si}(100)$ from $[\text{Ba}(\text{TDFND})_2\text{H}_2\text{O}]$

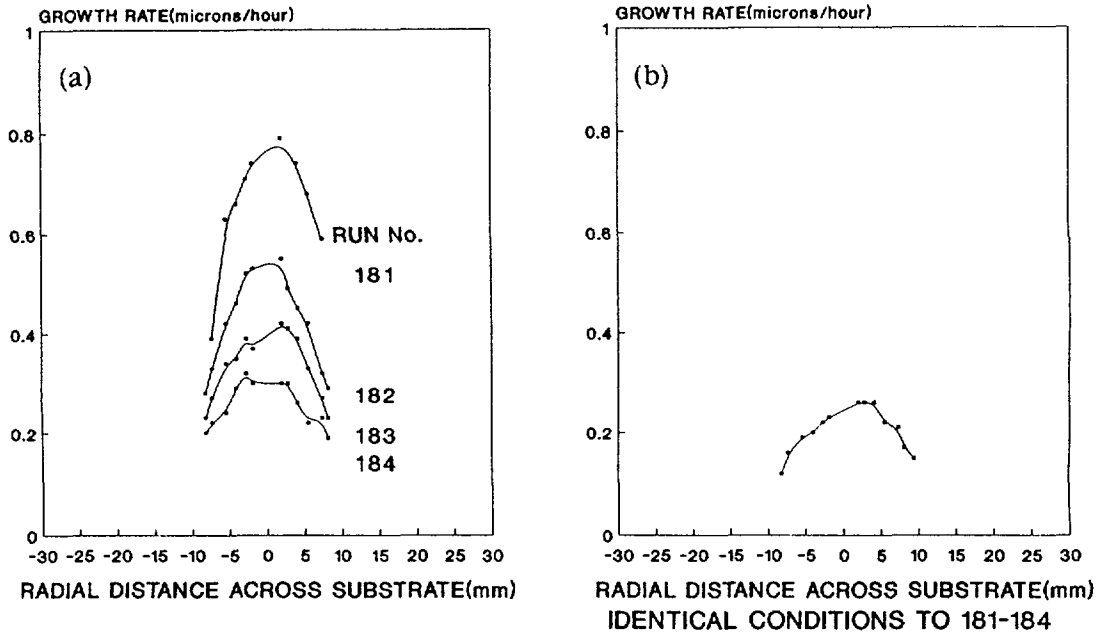


Figure 5 Layer thicknesses across the substrate for BaF₂ deposited on Si(100) at 730°C
 (a) from [Ba(TDFND)₂H₂O] with several runs using the same sample of precursor held at 160°C;
 (b) from [Ba(HFOD)₂H₂O] held at 160°C.