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RETENTION OF ^{210}Po BY REFRACTORY OXIDES

W.H. HALE

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Savannah River Laboratory

Aiken, South Carolina

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RETENTION OF ^{210}Po BY REFRACTORY OXIDES

by

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ABSTRACT

^{210}Po is released from the refractory oxide barium cerate at 800-1000°C by a volume diffusion process. BaCeO_3 is prepared by reacting CeO_2 with BaO or $\text{Ba}(\text{NO}_3)_2$ at 700°C, with BaCO_3 at 800°C, or with BaO_2 at 530°C.

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INTRODUCTION

^{210}Po is a radionuclide with some of the properties that are required for application as an isotopic power source. ^{210}Po has a high specific power and emits small amounts of penetrating radiation. The half-life of ^{210}Po is 138.4 days; decay is by alpha emission (5.408 Mev) to stable ^{206}Pb ; a 0.803 Mev gamma ray occurs in only $1.07 \times 10^{-3}\%$ of the transitions. Pure ^{210}Po has a specific power of 143 watts/g. However, because polonium metal melts at 254°C and has 1 atm vapor pressure at 962°C , it is unsuitable for high temperature applications.

A ^{210}Po power source must be stable in air at 1000°C for use in a thermoelectric power converter. Gadolinium polonide, infused in tantalum rings, has been proposed as the heat source in some space missions; the polonide is stable at 1000°C and compatible with tantalum. However, it reacts vigorously with air at ambient temperatures to evolve finely divided PoO_2 , and therefore could be hazardous if the containment capsule were breached. Polonium oxide, unlike lanthanide and actinide oxides, is volatile and, thus, not an acceptable fuel form.

Attempts to prepare refractory stoichiometric compounds of polonium were not successful. BaPoO_3 , analogous to the refractory BaTeO_3 , releases polonium at 900°C . Ba_3PoO_6 , analogous to Ba_3TeO_6 , could not be synthesized.

This report describes an attempt to stabilize BaPoO_3 in dilute solid solution with a refractory oxide of similar structure. The synthesis and polonium retention characteristics of barium cerate (BaCeO_3) and the synthesis of barium thorate (BaThO_3), are also described.

SUMMARY

^{210}Po was not retained in refractory oxide matrices at 800-1000°C. Experiments were designed to place BaPoO_3 , a perovskite-structure compound, in dilute solid solution with the perovskites, BaCeO_3 and BaThO_3 . Polonium was released from the BaCeO_3 lattice by a volume diffusion process in which polonium diffuses slowly through either individual grains or the entire lattice.

Methods for synthesizing barium cerate and barium thorate were developed. BaCeO_3 can be prepared by reacting CeO_2 with BaO or $\text{Ba}(\text{NO}_3)_2$ at 700°C, with BaCO_3 at 800°C, or with BaO_2 at 530°C. BaThO_3 can be prepared by reacting ThO_2 with BaO or BaCO_3 at 900°C.

DISCUSSION

Two binary oxides with the perovskite structure were selected as host lattices for ^{210}Po . Methods were developed for synthesizing the perovskites at the lowest possible temperature, and the ability of the oxides to retain polonium was determined by calorimetry and thermogravimetric analysis.

SELECTION OF AN OXIDE HOST MATRIX

A refractory binary oxide should contain Po^{4+} , the stable oxidation state at high temperature. Alkaline earth oxides are very stable and have high melting temperatures, and, in general, react with other metal oxides to form a refractory binary oxide. As shown in Figure 1,¹ the reaction of BaO with PoO_2 should produce BaPoO_3 with the cubic perovskite structure. Pure BaPoO_3 has been prepared and shown to be volatile at 900°C .²

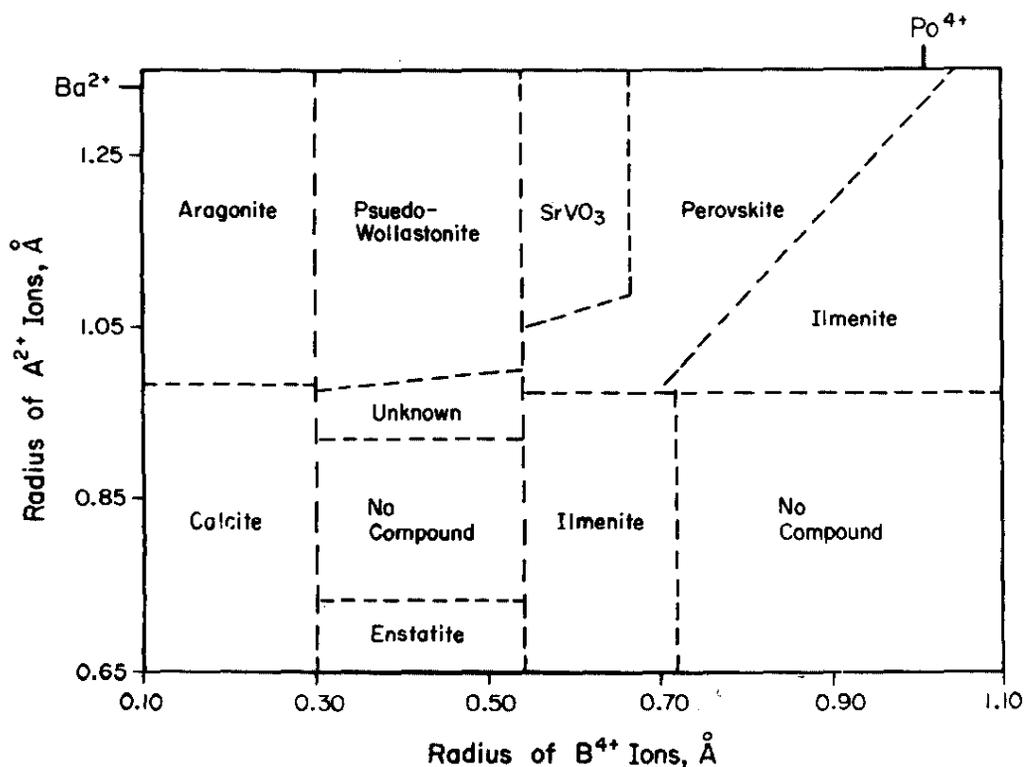


FIG. 1 CLASSIFICATION OF $\text{A}^{2+}\text{B}^{4+}\text{O}_3$ COMPOUNDS ACCORDING TO IONIC RADII

The perovskite crystal structure of $A^{2+}B^{4+}O_3$ compounds is shown in Figure 2. In the ideal cubic form of this structure, A has 12 oxygen neighbors. A polonium ion in the B position has 6 oxygen neighbors and should be resistant to further oxidation. A dilute solid solution of $BaPoO_3$ in $BaXO_3$ can be viewed as almost pure $BaXO_3$ with a few X^{4+} ions replaced by Po^{4+} (a "substitutional" solid solution). Ideally, Po^{4+} ions would be trapped in this matrix, greatly reducing the volatility of ^{210}Po at 900-1000°C.

Barium cerate and barium thorate satisfy the following criteria for maximum solubility with $BaPoO_3$:

- (1) The 4+ oxidation state of each element is stable at high temperature.
- (2) The ionic radii of Ce^{4+} and Th^{4+} are within 15% of that of Po^{4+} .
- (3) Both $BaCeO_3$ and $BaThO_3$ have the cubic perovskite structure.

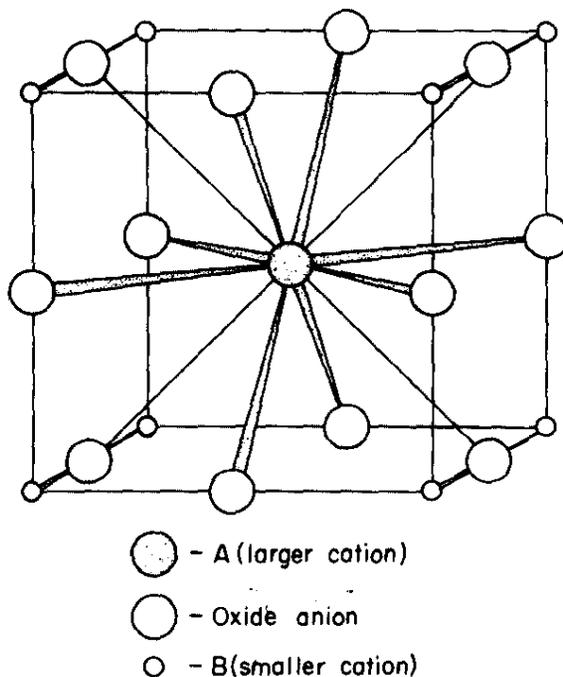


FIG. 2 PEROVSKITE CRYSTAL STRUCTURE OF $A^{2+} B^{4+}O_3$ COMPOUNDS

Barium was the only alkaline earth used in this work. The divalent ions of the other alkaline earths are too small to form a cubic perovskite with Po^{4+} , Ce^{4+} , or Th^{4+} . For an ABO_3 perovskite, the ionic radii are related by³

$$r_A + r_O = t \sqrt{2} (r_B + r_O) \quad (1)$$

where:

r_A = radius of the A^{2+} ion

r_B = radius of the B^{4+} ion

r_O = radius of the O^{2-} ion = 1.32 Å

t = tolerance factor

Compounds with t between 0.80 and 1.00 usually have the perovskite structure. For lower values of t the ilmenite structure is found. The calculated values of t for several combinations of alkaline earths and the $4+$ ions are given in Table I.

TABLE I

Calculated Values of the Tolerance Factor for ABO_3 Perovskites (ionic radii in parentheses)

	Tolerance Factor (A/B)		
	Po^{4+} (1.02 Å)	Th^{4+} (1.02 Å)	Ce^{4+} (0.94 Å)
Ba^{2+} (1.34 Å)	0.80	0.80	0.83
Sr^{2+} (1.12 Å)	0.74	0.74	0.76
Ca^{2+} (0.99 Å)	0.70	0.70	0.72

Thus, barium is the only alkaline earth that can form a perovskite-structure compound with polonium, cerium, or thorium.

PREPARATION OF BARIUM CERATE AND BARIUM THORATE

Experimental Procedure

Barium cerate and thorate were prepared by reacting several barium reagents with CeO_2 and ThO_2 . Preliminary work indicated that BaCeO_3 could be prepared at a lower temperature than BaThO_3 , minimizing the potential for loss of ^{210}Po during solid solution formation. Therefore, the synthesis of BaCeO_3 was studied in greater detail.

CeO_2 and ThO_2 were prepared by calcining the freshly prepared oxalates at 600°C for 5 hours. The sintered density of oxalate-produced CeO_2 pellets was about 1.5 times greater than that of CeO_2 pellets prepared by decomposing commercial cerous carbonate. The higher density indicates smaller particle size and thus a more reactive oxide. No difference in pellet density was observed between samples of thorium oxide obtained commercially and samples prepared by 600°C calcination of thorium oxalate or oxycarbonate.

The barium reagents were: (1) barium oxide, (2) barium carbonate (reagent grade), (3) barium nitrate (reagent grade), and (4) barium dioxide (technical grade).

In every case, reactants were mixed well, pelletized, and fired at the appropriate temperature. The powdered reactants (usually equimolar amounts) were mixed at high speed for 5 minutes in a Spex "Mixer/Mill,"* Model 5000. About 10 mg of the mixed reactants were pressed into a pellet at 20 kpsi in a lubricated stainless steel die (0.19-in. diameter). Inclusion of 0.2 wt % polyethylene glycol binder strengthened the pellets. The pellets were placed on platinum plates and fired in air in either a tube or muffle furnace. For thermogravimetric analysis, pellet chips were placed in a platinum sample holder.

* Registered tradename of Spex Industries Inc.

Thermogravimetric data were obtained with an Ainsworth recording semimicro vacuum balance and a Marshall single-zone 1200°C tubular furnace. At a constant heating rate, both weight and the derivative of weight with respect to time were continuously recorded as a function of time. Evolved gases were determined with an in-line Associated Electronics Industries MS-10 mass spectrometer. A vacuum of 10^{-6} - 10^{-5} torr was obtained with a 300 ℓ /sec oil diffusion pump and a 425 ℓ /sec mechanical pump. Some data were also obtained with an R. L. Stone, TGA Model 5B system.

Reaction products were analyzed by X-ray diffraction. Chips of the fired pellets were ground and loaded into capillary tubes for powder pattern measurement. A standard lattice constant program⁴ was used to calculate lattice constants from 2θ values with the IBM 360 computer.

Reaction of BaO With CeO₂ and ThO₂

Barium cerate was prepared by heating equimolar amounts of BaO with CeO₂ at 700°C for 16 hours; barium thorate was prepared at 900°C from BaO and ThO₂. Pellets were fired in air at several different temperatures and the percentage reaction estimated from the X-ray powder pattern. These reactions cannot be studied by thermogravimetric analysis because no weight loss is involved.

TABLE II
Reactions of BaO with CeO₂ and ThO₂

<u>Reactants</u>	<u>Time, hr</u>	<u>Temperature, °C</u>	<u>% Conversion to Product</u>
BaO-CeO ₂	16	600	0
	16	700	~98
	16	750	100
	16	800	100
	16	900	100
BaO-ThO ₂	16	700	0
	16	800	~10
	16	900	~95

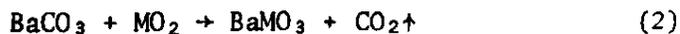
The products were identified by demonstrating that the interplanar spacings (d values) fit a cubic crystal system and by comparing the experimental lattice constants with those previously reported.^{1,5} The data shown in Table III were averaged from six BaCeO₃ and five BaThO₃ products. The lattice constant of BaPoO₃ is 4.468 Å.

TABLE III
X-Ray Powder Patterns of BaCeO₃ and BaThO₃

Miller Index	BaCeO ₃		BaThO ₃	
	d, Å	Relative Intensity	d, Å	Relative Intensity
110	3.090	10	3.179	10
200	2.192	4	2.246	4
211	1.789	9	1.832	8
220	1.550	3	1.589	2
310	1.387	4	1.422	4
222	1.268	1	-	0
321	1.173	3	1.201	5
400	1.103	1	1.123	1
Lattice Constant, Å	4.410 ±0.003		4.511 ±0.004	
Previously Reported	4.387 ¹		4.48 ⁵	

Reaction of BaCO₃ With CeO₂ and ThO₂

Barium carbonate reacts with CeO₂ and ThO₂ with evolution of CO₂.



Since pure BaCO₃ does not decompose below 1000°C, weight loss below 1000°C indicates that the reaction is occurring; the course of the reaction can be followed with thermogravimetric analysis. In preliminary work, pellets of BaCO₃-CeO₂ and BaCO₃-ThO₂ were fired in air for 16 hours. BaCeO₃ was formed at 850°C; BaThO₃, at 900°C.

Thermograms of $\text{BaCO}_3\text{-CeO}_2$ pellets showed a single weight loss period corresponding to BaCeO_3 formation. When pellets were heated in static air at $10^\circ\text{C}/\text{min}$, reaction began at 820°C and was nearly complete at 1080°C (Figure 3). In vacuum, reaction began at 800°C and was only $\sim 75\%$ complete at 1080°C . Because the reaction did not proceed faster in vacuum, diffusion of CO_2 through either the entire pellet or individual grains must be the rate-determining process. Mass spectrometry confirmed that CO_2 was evolved during the weight loss period. Activation energy for the reaction was 34 kcal/mole in vacuum and 26 in air.

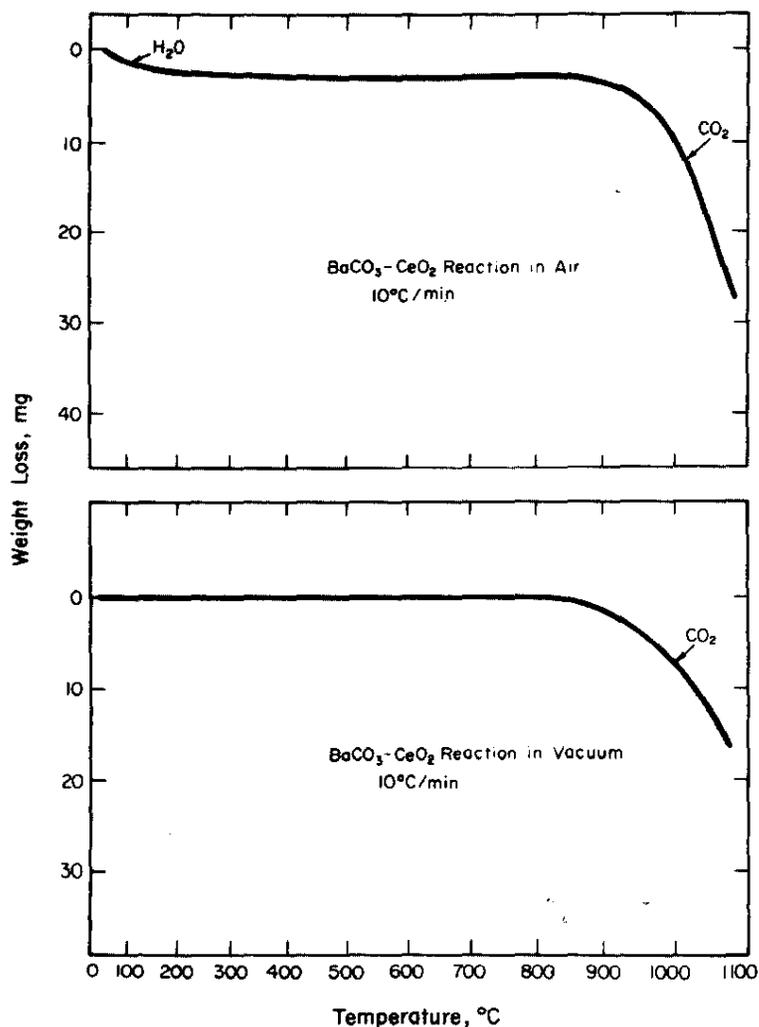


FIG. 3 THERMOGRAMS OF $\text{BaCO}_3\text{-CeO}_2$ REACTIONS

Reaction of $\text{Ba}(\text{NO}_3)_2$ With CeO_2

Barium nitrate decomposes to BaO which then reacts with CeO_2 . Weight loss from a $\text{Ba}(\text{NO}_3)_2$ - CeO_2 pellet, heated in static air at $10^\circ\text{C}/\text{min}$, began at 550°C and ended at 830°C (Figure 4). In vacuum, weight loss from a similar pellet began at 500°C and ended at 800°C . However, pure $\text{Ba}(\text{NO}_3)_2$ also began to lose weight in vacuum at 500°C .

To determine if BaCeO_3 was formed during the weight loss period, $\text{Ba}(\text{NO}_3)_2$ - CeO_2 pellets were fired in air for 18 hours at 600 , 700 , and 800°C . X-ray diffraction showed only traces of BaCeO_3 produced at 600°C but complete formation at 700 and 800°C .

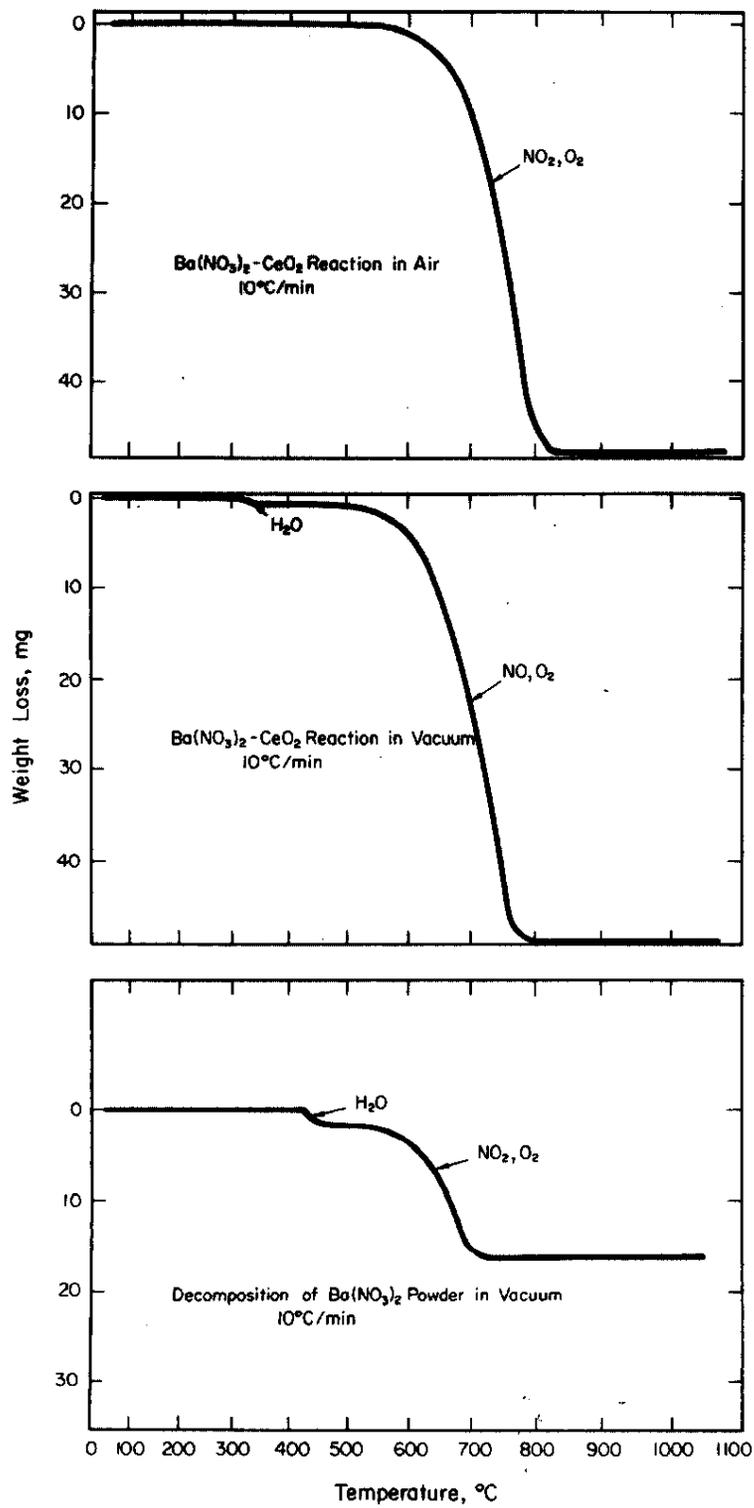


FIG. 4 THERMOGRAMS OF $\text{Ba}(\text{NO}_3)_2$ - CeO_2 REACTIONS AND $\text{Ba}(\text{NO}_3)_2$ DECOMPOSITION

Mass spectrometry at a pressure of 2×10^{-5} torr showed that NO and O₂ were evolved during the weight loss period, as shown in Equation 3.



In air, NO would be immediately oxidized to NO₂. Activation energy for the Ba(NO₃)₂-CeO₂ reaction in vacuum was 31 kcal/mole.

Reaction of BaO₂ With CeO₂

Thermograms of BaO₂-CeO₂ pellets showed two distinct weight loss periods, the second one corresponding to BaCeO₃ formation according to Equation 4.



For pellets heated at 10°C/min in static air, the two reaction periods occurred at 25-320°C and 515-630°C (Figure 5). In vacuum, reaction temperatures were lowered to 25-200°C and 350-500°C. Pure BaO₂ showed no decomposition up to 750°C.

To determine which weight loss period corresponded to BaCeO₃ formation, BaO₂-CeO₂ pellets were fired in air for 24 hours at several temperatures. No BaCeO₃ was formed at 250 and 400°C (first weight loss period in air); BaCeO₃ formation was complete at both 530 and 700°C (second period).

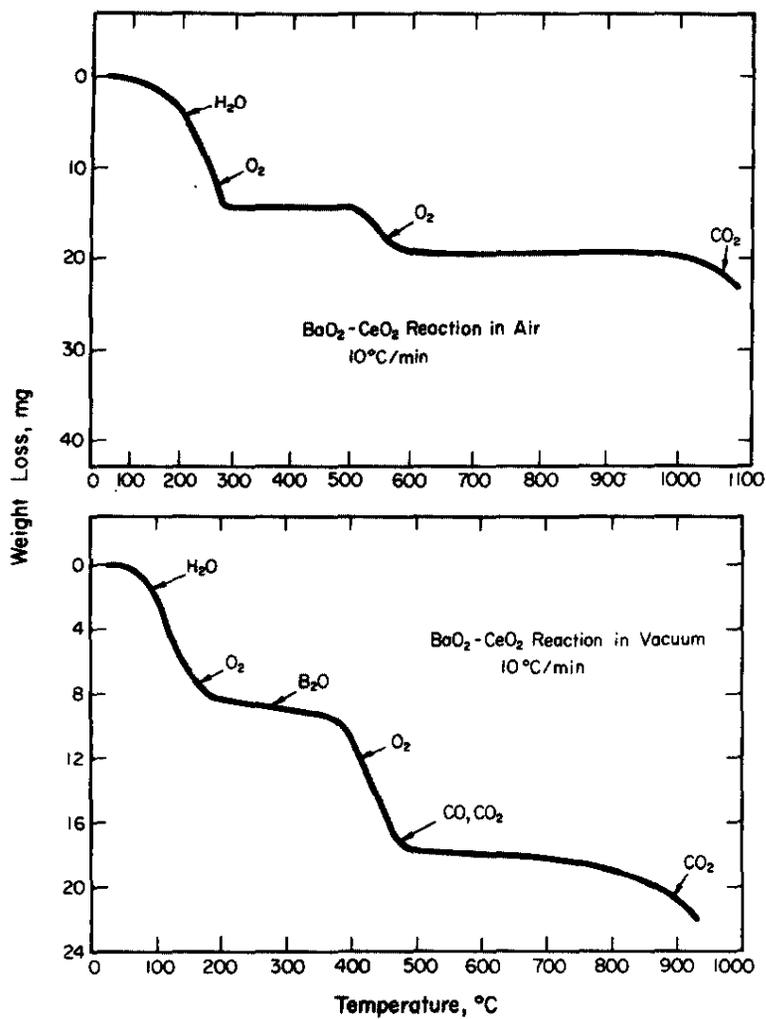


FIG. 5 THERMOGRAMS OF BaO₂-CeO₂ REACTIONS

The complex differential thermogram (Figure 6) showed that each major weight loss period included at least two reactions. Mass spectrometry showed that H₂O was the primary species evolved in the first portion of the first weight loss period. The activation energy was 10 kcal/mole, a value typical of evolution of gaseous H₂O from pellets. The second portion of this period was evolution of O₂, possibly from the decomposition of BaO₄, a common impurity in technical-grade BaO₂. Activation energy for the first portions of the second weight loss period (BaO₂-CeO₂ reaction) was 34 kcal/mole.

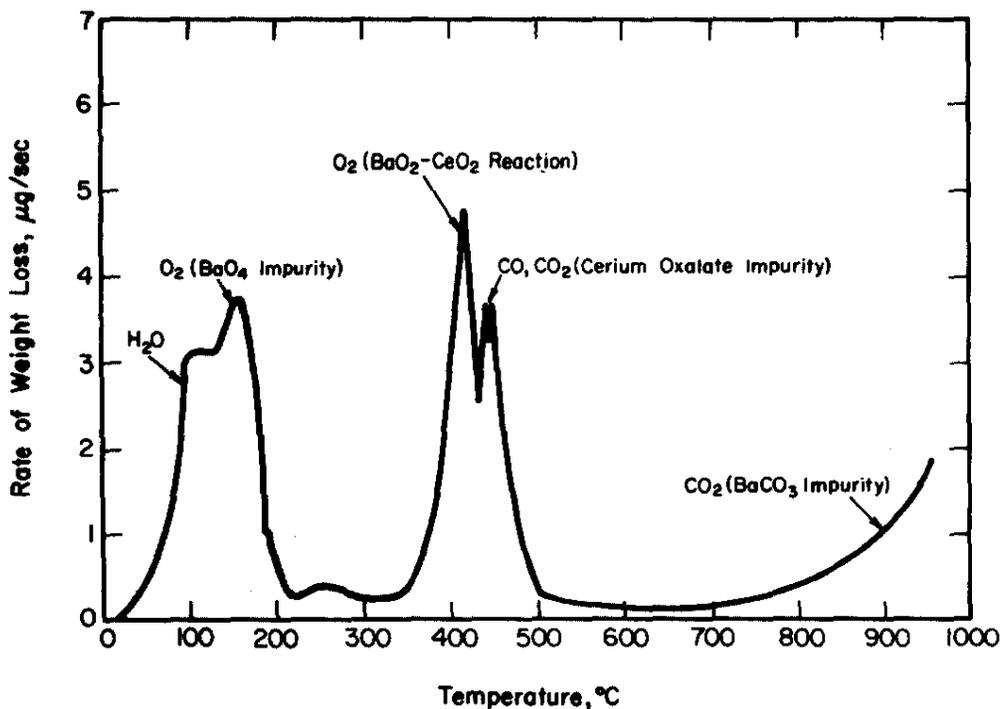


FIG. 6 DIFFERENTIAL THERMOGRAM OF BaO₂-CeO₂ REACTION IN VACUUM

The latter portion of this period was evolution of CO, CO₂, and H₂O, probably from decomposition of residual cerium oxalate. CO₂ was evolved during the high temperature weight loss period, indicating reaction of CeO₂ with BaCO₃ impurity.

RETENTION OF POLONIUM BY OXIDE MATRICES

No conditions were found under which polonium could be retained in BaCeO_3 or $\text{BaO-ThO}_2\text{-PoO}_2$ matrices at 1000°C . In preliminary work, three Po-containing pellets were fired at various temperatures and analyzed for polonium retention and extent of reaction. Polonium retention characteristics of both matrices were determined more accurately when contained TGA equipment became available. One pellet of each matrix was studied with TGA.

BaCeO_3 can be prepared at 700°C in a $\text{BaO-CeO}_2\text{-PoO}_2$ mixture without loss of polonium. However, polonium is released in the critical temperature range $800\text{-}1000^\circ\text{C}$. That the chemical form of polonium at this point could not be determined is not important for these reasons: (1) If PoO_2 has not reacted at 800°C , it escapes from the lattice before the solid solution has been formed. (2) If the $\text{BaCeO}_3\text{-BaPoO}_3$ solid solution exists at 800°C , BaPoO_3 decomposes upon subsequent heating and escapes from the lattice, probably as PoO_2 . Because the temperature required to prepare BaThO_3 is high, PoO_2 escapes from the lattice before a solid solution can be formed.

Polonium-containing pellets were prepared by techniques similar to those described earlier. ^{210}Po metal, deposited on platinum gauzes, was purchased from Mound Laboratory. Polonium was dissolved from the gauzes in concentrated HNO_3 and precipitated as Po(OH)_4 by the addition of concentrated NH_4OH . The solution was filtered through a fine-pore glass frit, and the hydroxide cake was rinsed with $1\text{M NH}_4\text{OH}$. The hydroxide was transferred to a platinum dish and allowed to stand overnight while Po(OH)_4 was self-calcined to PoO_2 . PoO_2 was mixed with appropriate amounts of the barium and cerium or thorium reagents in the Spex "Mixer/Mill." The mixture was pressed into a pellet at 20 kpsi. Pellets were placed on platinum plates and fired in steel containers, or placed in platinum pans for TGA studies.

After the pellets were fired, the extent of reaction to BaCeO_3 or BaThO_3 was determined by X-ray diffraction analysis of the pellet surface. The pellet was rotated on a "Norelco"* wide-range goniometer during measurement. Because polonium was present in small amounts, conversion of PoO_2 to BaPoO_3 could not be determined. Polonium content before and after firing was determined with a milliwatt twin-bridge calorimeter.

The pellets were analyzed by thermogravimetric analysis with the Ainsworth balance - MS-10 mass spectrometer system described earlier.

* Registered tradename of Philips Electronic Instruments.

Pellet 1

Pellet 1 contained 0.674 mmole BaCO_3 , 0.678 mmole CeO_2 , and 0.057 mmole PoO_2 (11.91 mg ^{210}Po). The pellet was fired in a tightly closed steel container at 800°C for 24 hours. A small container of CaO was placed next to the pellet to act as an absorber for CO_2 , the reaction product.

The fired pellet contained 10-20% BaCeO_3 and only 9.5% of the original ^{210}Po . The CaO powder fluoresced orange, indicating at least partial sorption of ^{210}Po . X-ray diffraction of the powder showed only CaO . PoO_2 , with a vapor pressure of ~ 0.6 torr at 800°C , volatilized from the pellet.

Pellet 2

Pellet 2 contained 1.091 mmole BaCO_3 , 0.993 mmole ThO_2 , and 0.040 mmole PoO_2 (8.48 mg of ^{210}Po). The pellet was fired in a tightly closed steel container at 900°C for 20 hours.

The fired pellet contained no BaThO_3 and only 9.8% of the original ^{210}Po . Most of the polonium was adsorbed on the steel vessel walls, which had a blue fluorescence. The vapor pressure of PoO_2 is ~ 6 torr at 900°C .

The formation of BaThO_3 was probably prevented by the accumulation of CO_2 reaction product. If the vessel remained tightly closed, and all BaCO_3 reacted, the partial pressure of CO_2 would be ~ 7 atm.

Pellet 3

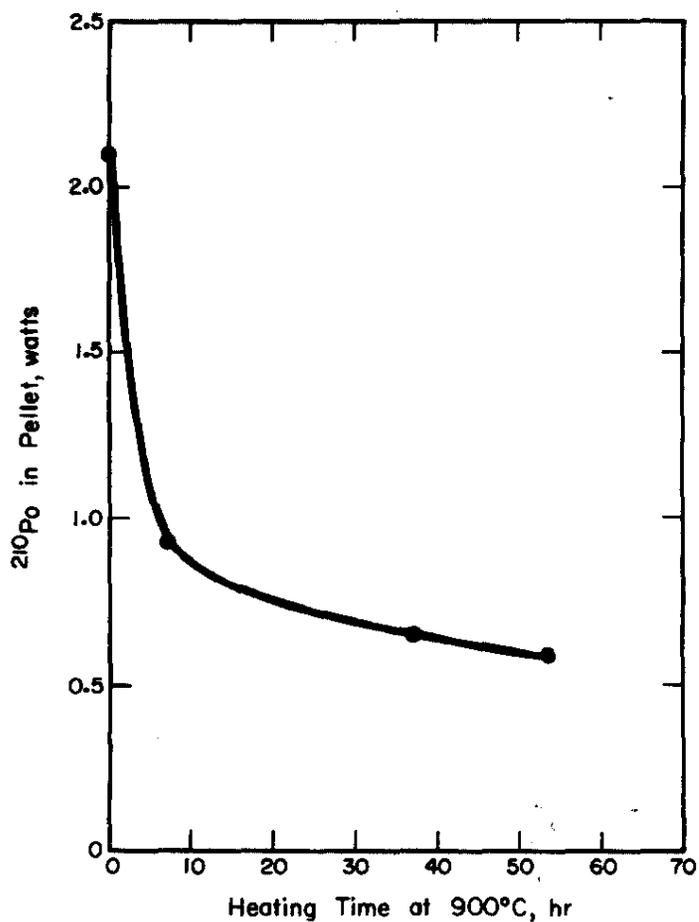
Pellet 3 contained 1.233 mmole BaCO_3 , 1.134 mmole CeO_2 , and 0.089 mmole PoO_2 (18.6 mg ^{210}Po). The pellet was fired at 850°C for 18 hours in a steel container. The container had a loose fitting top to allow CO_2 to escape but minimize the release of ^{210}Po into the gloved box. The fired pellet contained $\sim 70\%$ BaCeO_3 and 79% of the original ^{210}Po .

As a test of the thermal stability of the ^{210}Po solid solution, the fired pellet was heated to 900°C in a platinum boat inside a capped steel pipe. Both ends of the pipe protruded from the furnace to provide a cold trap for any polonium evolved from the pellet. As shown in Table IV and Figure 7, 72% of the ^{210}Po was evolved at a decreasing rate. The power density decreased from 23.4 to 6.6 watts/cm³ at a mass density of 4.4 g/cm³ (about half the theoretical density of crystalline barium cerate).

TABLE IV

 ^{210}Po Release from a BaCeO_3 Matrix at 900°C

<u>Time at 900°C, hr</u>	<u>^{210}Po, watts</u>	<u>% of original ^{210}Po remaining in pellet</u>
0	2.097	100
7	0.925	44.1
37	0.647	30.9
53	0.586	27.9

FIG. 7 RELEASE OF ^{210}Po FROM PELLETS OF BARIUM CERATE

Pellet 4

At the time Pellet 4 was prepared, it contained 0.571 mmole BaO, 0.524 mmole ThO₂, and 0.063 mmole PoO₂ (13.2 mg ²¹⁰Po). 87% of the ²¹⁰Po had decayed to ²⁰⁶Pb when polonium release was studied by TGA.

The purpose of this test was to analyze the polonium retention characteristics of a BaO-ThO₂-PoO₂ mixture under the adverse conditions of vacuum and high rate of heating and to compare the data with a BaCeO₃-BaPoO₃ mixture heated under favorable conditions (Pellet 5). To permit mass spectrometry, pellet 4 was heated in vacuum ($\sim 10^{-5}$ torr) rather than the favorable oxygen atmosphere; the heating rate was 3°C/min, and reaction of the oxides to the perovskite compounds was probably incomplete.

The ordinary and differential thermograms are shown in Figure 8. H₂O and CO₂ (from BaCO₃ impurity) were identified by mass spectrometry. Activation energies for the release of H₂O and CO₂ were 8.4 and 34.2 kcal/mole, respectively. These values agree closely with data obtained in the earlier work with BaO₂-CeO₂ and BaCO₃-CeO₂ pellets.

The Po and Pb portions of the weight loss curve were assigned according to the known Po/Pb ratio. No ions corresponding to doubly charged Po or Pb species were observed in the mass spectrum (the spectrometer is limited to m/e ratios ≤ 200). Release of ²¹⁰Po was observed at $\sim 850^\circ\text{C}$ with an activation energy of 39.0 kcal/mole. The initial release temperature was probably lower, but was obscured in the CO₂ weight loss. Evolution of lead began at $\sim 960^\circ\text{C}$. The temperature was maintained at 960°C until constant weight was attained. After this experiment, the quartz tube surrounding the sample holder had an intense violet fluorescence, confirming that ²¹⁰Po had been released.

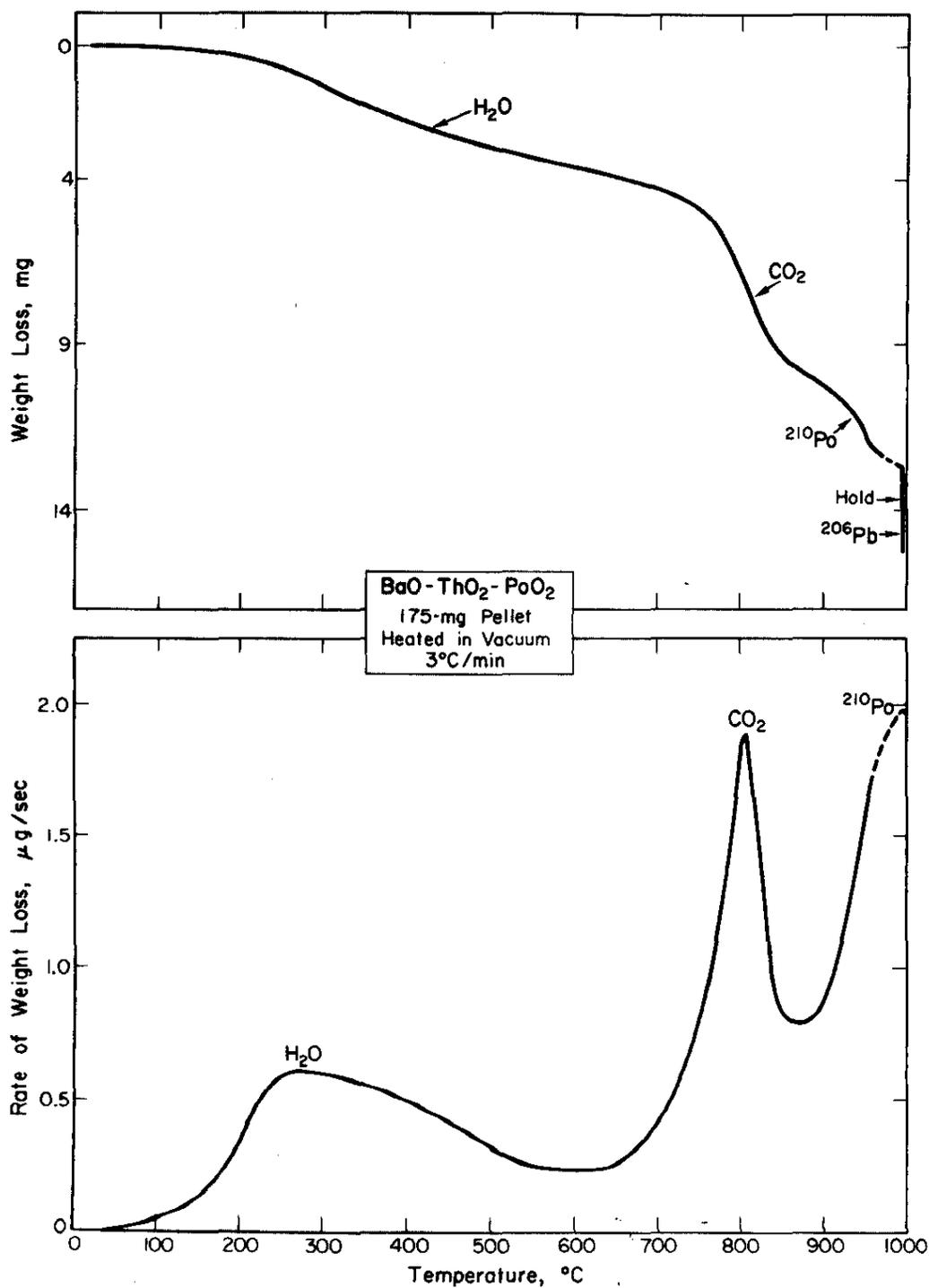


FIG. 8 THERMOGRAMS OF ^{210}Po RELEASE FROM A $BaO-ThO_2-PoO_2$ PELLETT

Pellet 5

At the time Pellet 5 was prepared, it contained 0.571 mmole BaO, 0.524 mmole CeO₂, and 0.031 mmole PoO₂ (6.45 mg ²¹⁰Po). 87% of the ²¹⁰Po had decayed when the thermogravimetric analysis was made.

The solid solution was prepared by heating the pellet to 700°C at 3°C/min in a flowing stream of 20% oxygen - 80% helium (thermogram shown in Figure 9). The temperature was maintained at 700°C for 20 hours. As shown earlier, these conditions are sufficient for reaction of the oxides to form BaCeO₃ and BaPbO₃.⁹ A minimum temperature for formation of BaPoO₃ has not been determined.

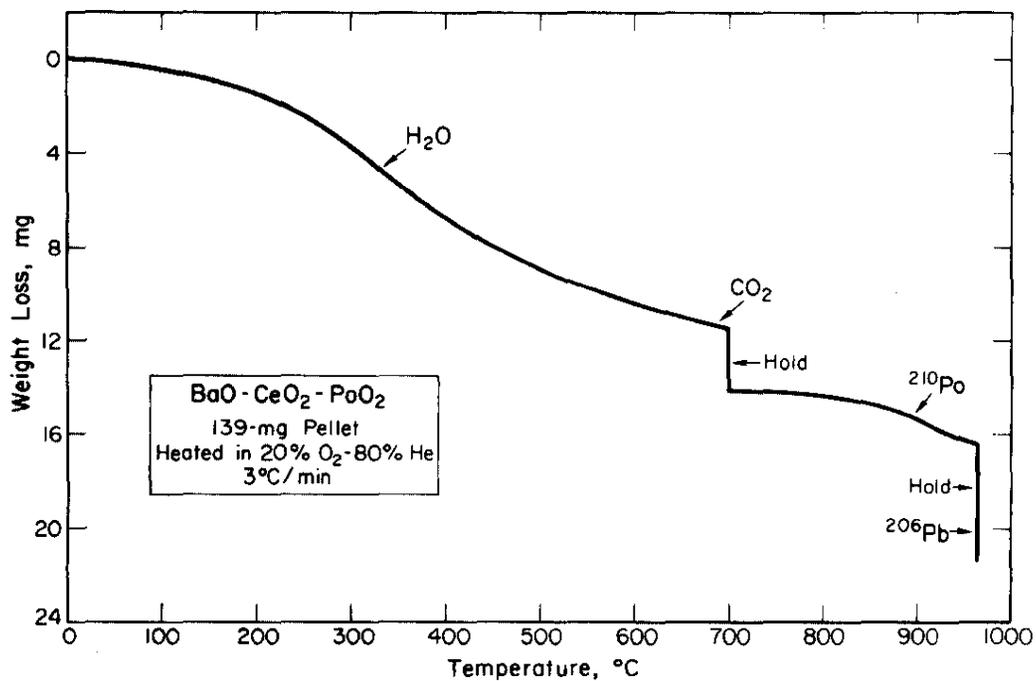


FIG. 9 THERMOGRAM OF ²¹⁰Po RELEASE FROM A BaCeO₃ PELLETT

By analogy with Pellet 4, the first two weight loss periods were assigned to H₂O and CO₂. The pellet attained a constant weight during the 20-hour heating period indicating complete removal of H₂O and CO₂. No fluorescence was observed in the quartz tube after this heating period.

²¹⁰Po release began at ~800°C with an activation energy of 45 kcal/mole, significantly higher than from the BaO-ThO₂-PoO₂ pellet. ²⁰⁶Pb release began at ~910°C with an activation energy of 50 kcal/mole. The lead release gave 82% of the high temperature weight loss compared to the theoretical 87%. ²¹⁰Po release was again confirmed by violet fluorescence in the quartz tube.

Release of Po and Pb from the pellet occurred by a volume diffusion process, as determined by holding the temperature constant at 965°C and determining the functional dependence of weight loss with time.⁷ The data were fitted to an equation of the form

$$W = Kt^{1/2}$$

where

W = weight loss, mg

K = rate constant = 0.71 mg/min^{1/2}

t = time, min

Since weight was lost before the constant temperature was reached and an arbitrary time zero could not be chosen, trial plots of weight loss versus the logarithm of time were made until a linear dependence with slope 1/2 was found. The resulting plot of the weight loss data using the time zero obtained in the trial plots is shown in Figure 10. Volume diffusion is the rate limiting process through 76% of the weight loss period; weight loss then becomes linear with time indicating that vaporization within the pellet is rate limiting.⁷

A volume-diffusion process can arise from two mechanisms, diffusion across a thickening depleted layer in the pellet or diffusion across layers in individual grains followed by rapid pore diffusion throughout the pellet. More experiments would be needed to determine the mechanism in this case.

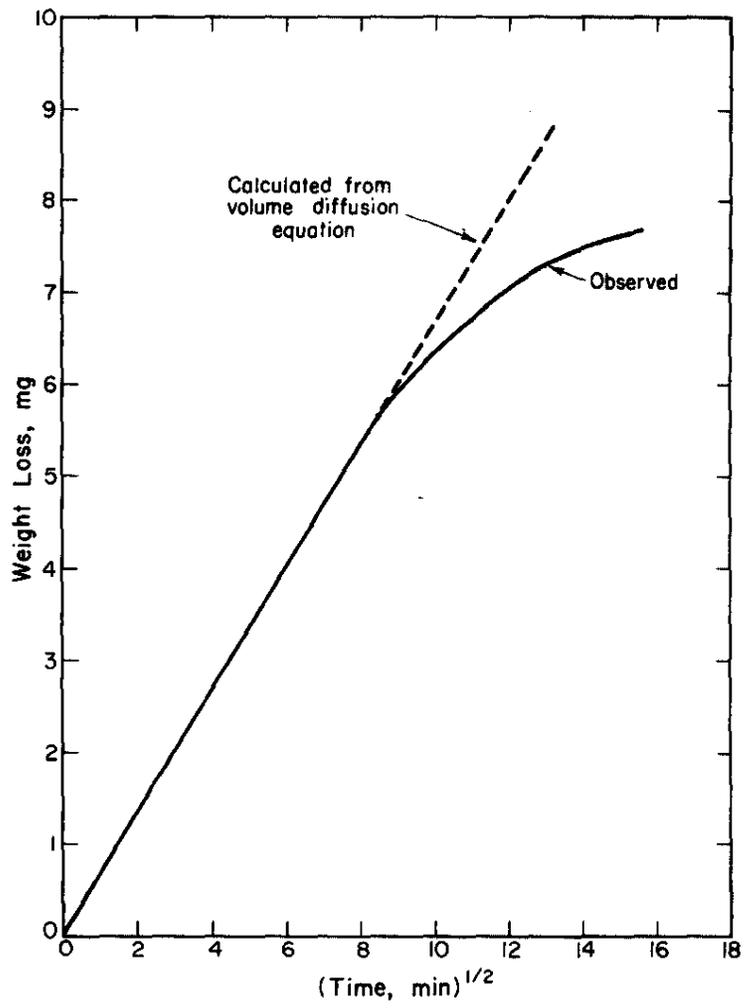


FIG. 10 Po-Pb WEIGHT LOSS FROM A BaCeO₃ PELLETT AT 965°C

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