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Report No. IITRI-U6038-10
(Final Technical Report)

DOPING STUDY OF LIGHT METAL BASED FUELS

E. S. Freeman and A. Becker

December 1966

Air Force Rocket Propulsion Laboratory
Research and Technology Division
Edwards Air Force Base, California
Air Force Systems Command, United State Air Force

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FOREWORD

This is Report No. IITRI-U6038-10, the Final Technical Report on IITRI Project U6038, Contract No. AF04(611)-11386, entitled "Doping Study of Light Metal Based Fuels. This report covers the period from January 3, 1966 through October 4, 1966.

This program was conducted by IIT Research Institute, 10 West 35th Street, Chicago, Illinois, for the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California, under Air Force Program Structure No. 750G, AFSC Project No. 3148, and AFSC Task No. 3148. The program monitor for this project was 1st Lt. William H. Summers of Edwards Air Force Base, California.

The program was under the direction of Dr. Eli S. Freeman, Assistant Director, Chemical Sciences Research, the experimental work was performed by Mr. Aaron J. Becker, Assistant Chemist, and Mr. John Petersen, Technician.

Data include in this report are recorded in Logbook No. 16855.

The copy of the final report sent to the sponsor contains an Appendix showing a colored photograph of the ignition of the doped LMH-2 powder.

This technical report has been reviewed and is approved:

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

ABSTRACT

The effects of doping on the chemical reactivity of beryllium and LMH-2 with respect to combustion was studied by means of differential thermal analysis (DTA). Specifically, the effects of doping with impurities on combustion was explored to determine if it is possible to increase the ignitibility of the fuels of interest. It was found that when beryllium and LMH-2 were heated under conditions of linearly increasing temperature from room temperature to 800°C in dry oxygen ignition did not take place. Under the same experimental conditions ignition occurred when the materials were doped with various metal fluorides or fluoro-silicates. The ignition temperature varied depending on the dopant impurity used. When an oxygen atmosphere saturated with water vapor in place of dry gas was used the reactivity of both fuels increased markedly. The exothermal decomposition of ammonium perchlorate was also observed to be catalyzed by some fluoride additives. Mixtures composed of the doped and undoped fuels and ammonium perchlorate were also investigated.

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DOPING STUDY OF LIGHT METAL BASED FUELS

SECTION I

INTRODUCTION

The standard heat of formation of BeO is -143.1 kcal/mole and its heat of combustion per unit weight is markedly higher than presently used propellant fuels. The use of beryllium as a fuel should represent a major step forward in high energy propellants, however, the relative low rate and inefficient combustion of this fuel is a major obstacle to realizing the full potential of this fuel. In previous work by Freeman and Anderson[1] it was found that doping with impurities can significantly increase the reactivity of fuels such as aluminum and more recently it was shown by Freeman and Becker[2] that this was also true for boron. The purpose of this present program was to conduct an exploratory study to determine if it is possible to increase the ignitibility and reactivity of beryllium and LMH-2 by doping.

Macek[3] et al, reported that the combustion of beryllium powder proceeds only under high pressures of oxygen and only at very high temperatures. This was attributed to the protective nature of the oxide layer. To increase the degree of oxidation it was suggested that the material must be heated to at least the boiling point of the oxide. The oxide melts at 2520°C and boils near 4000°C which accounts for Macek's observation that self sustained ignition takes place in beryllium powder only when a flame temperature of 4000°C or higher was obtained.

Terem[4] has heated beryllium powder to 1200°C as part of a study of the kinetics of oxidation of beryllium powder and did not observe ignition. However, he did find that water vapor strongly catalyzed the oxidation of beryllium.

Other workers have performed corrosion studies on bulk pieces of the metal. Cubicciotti[5] found the parabolic rate law was followed during oxidation and the activation energy calculated for the reaction was 62 kcal/mole. Gulbransen and Andrew[6] obtained results which disagree with Cubicciotti's. They found beryllium oxidizes in two steps, the first with an activation energy of 8.5 kcal/mole and the succeeding step with an activation energy of 50.3 kcal/mole.

Little work has been done on the physico-chemical characteristics of LMH-2 although it was synthesized in the high purity form (96%) in 1954. Reports on its chemistry are very scant in the literature and only within the past 6 years has their been definite proof of its structure. Experimental data on its combustion characteristics has not been published in the open literature.

SECTION II

EXPERIMENTAL

Materials

Information on the doping agents used in this program is listed in Table 1. The beryllium was obtained from Brush Beryllium Corporation and the LMH-2 from Ethyl Corporation. CP grade ammonium perchlorate was purchased from the City Chemical Company of New York. The oxygen and argon used in this program were purchased from Linde Division of Union Carbide with purities of 99.99% and 99.996% respectively.

The $AlF_3 \cdot 3KF$ and $AlF_3 \cdot KF$ were prepared at this Institute. The procedure involved heating $Al_2F_6 \cdot XH_2O$ and KF in the molar ratios indicated in the stoichiometric formula at 10°C/min in a DTA experiment. The endotherm for the reaction was at 650°C.

Apparatus and Procedures

The experiments in a pure oxygen atmosphere used sample weights of 75 mg of beryllium (average particle size 12μ), or 50 mg of LMH-2.

The LMH-2 was sieved and the 100/200 mesh samples were used but in all other respects the same experimental procedures were employed for both materials. 5 ± 2 weight percent of dopant was physically mixed with each of the fuels. The variation in amount of dopant used can be attributed to the very small weights of sample and dopant involved in the experiments. Samples were weighed into Vycor test tubes which were then placed into the DTA apparatus illustrated in Figure 1.

The ammonium perchlorate was pulverized and sieved into close screen fractions. The 270/325 and 100/120 sieve fractions were used in the experiments.

The differential thermal analysis (DTA) apparatus was specially adapted for this program. (Figure 1) The arrangement involved the use of an Inconel block located in the core of a resistance furnace. There were two holes in the block for Vycor test tubes which contained the sample and reference materials, respectively, and a third hole close to the edge of the block for a thermocouple to monitor the heating rate. The DTA thermocouples come up through the bottom of the block into the holes which contain the sample and reference tubes. The sample and reference tubes sit on the thermocouples. Small indentations were centered in the bottom of the tubes for the

Table 1

SOURCE AND PURITY OF FLUORIDE AND FLUOROSILICATE DOPANTS

Material	Source	Grade
Ammonium Fluoride	City Chemical-New York	Purified
Aluminum Fluoride	General Chemical	Reagent
Calcium Fluorosilicate	City Chemical-New York	Purified
Lead Fluoride	General Chemical	Purified
Lithium Fluoride	City Chemical-New York	Reagent
Lithium Fluorosilicate	City Chemical-New York	Reagent
Magnesium Fluorosilicate	Davison Chemical	20
Potassium Fluoride	General Chemical	Reagent
Silver Nitrate	General Chemical	Reagent
Sodium Iodide	General Chemical	Reagent

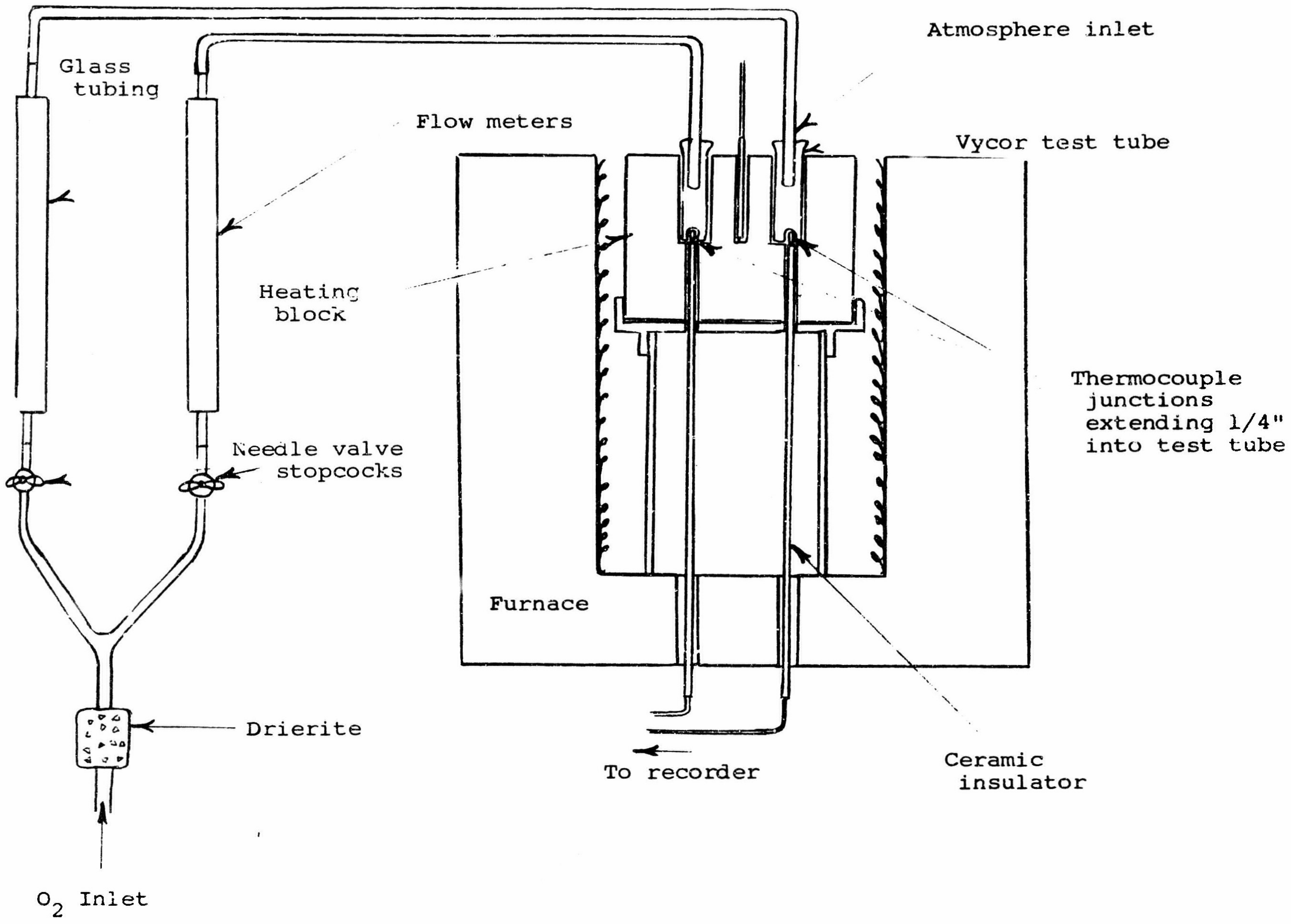


Figure 1

DTA System

thermocouples. The gases were introduced through tubes located directly in the mouth of the sample and reference vessels to provide the gaseous environment required for the experiment. Chromel-Alumel 28 gauge wires were used for the thermocouples in all the work.

In order to minimize the effects of water vapor on the reactions, the oxygen was passed over drierite prior to being passed over the sample. To determine the catalytic effects that water vapor may have on the reaction, oxygen was passed through a gas bubbler containing water, prior to passing it over the sample. In the experiments which necessitated the use of argon, the gas was also dried over drierite as in the case of oxygen. In all work with gases the flow rates were maintained at 300 ml/min and monitored with calibrated flow meters.

The heating rate used in all of the experiments was 10°C/min. A 7030A Mosely X-Y recorder was used to relate the differential temperature (Y-axis) to the reference temperature (X-axis). The differential termperature was taken as the difference between the sample temperature and an inert reference material. In the experiments on beryllium and LMH-2 in oxygen the recorders were calibrated for readouts of 4.1 millivolts per inch ($\approx$ 100°C/in) on the X-axis and 2.0 millivolts per inch on the Y-axis. The X-Y recorders were adjusted to give a readout of 0.1 mv per inch on the Y-axis for the experiments with ammonium perchlorate.

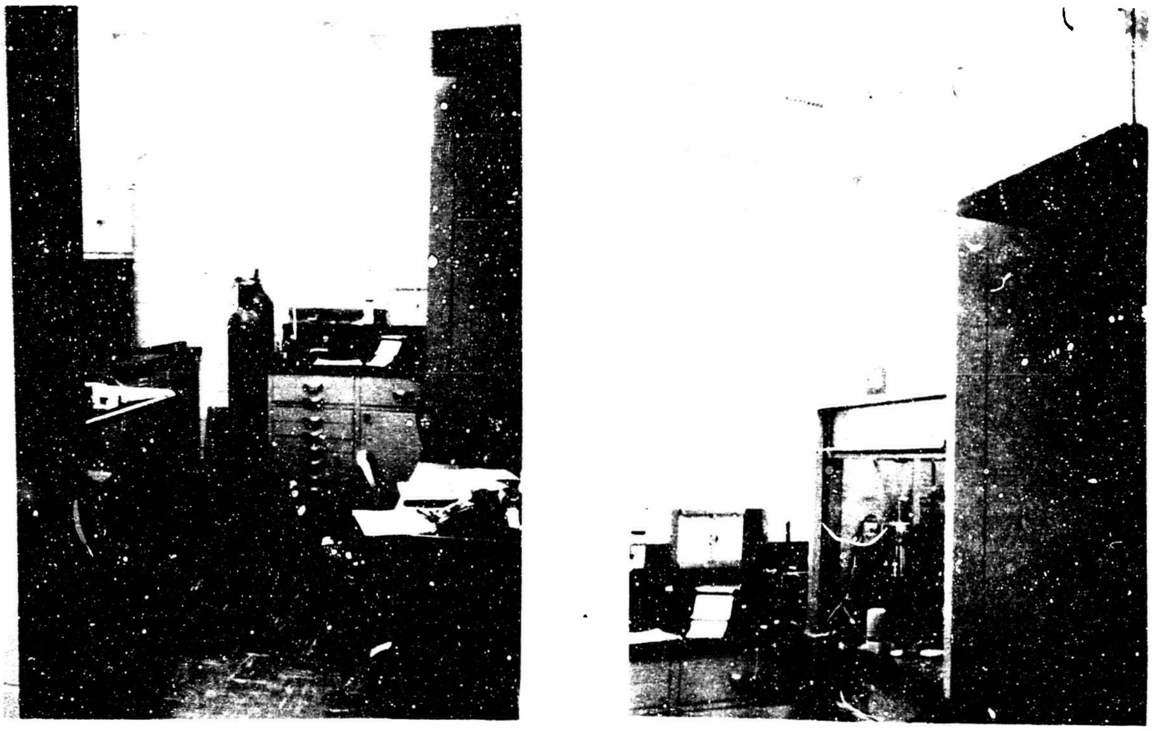
Photographs of the beryllium laboratory are shown in Figure 2. All of the experimental work was performed in this laboratory.

Results and Discussion

Beryllium

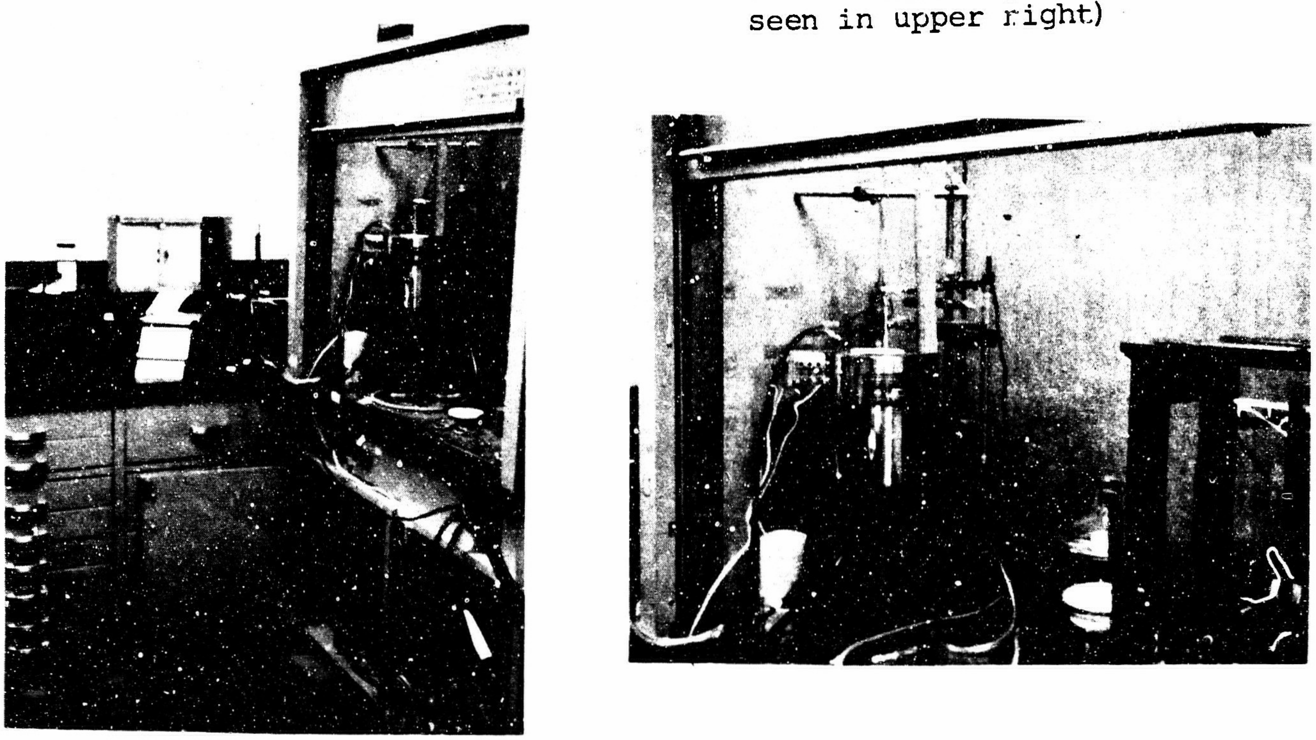
Figure 3 shows the differential thermal analysis curves of both doped and undoped beryllium samples heated in an oxygen atmosphere. The DTA curve for the undoped sample over the temperature range of 25°C to 1050°C is seen in Curve 1. The undoped beryllium did not ignite or even undergo rapid combustion. This is indicated by the apparent absence of exothermal DTA bands. As a standard procedure the sample was weighed before and after every DTA run. A gain in sample weight of the undoped beryllium was measured which indicated that oxidation took place during the DTA experiment. The extent of oxidation, however, was less than 40% of the predicted stoichiometric value, of the following reaction:

$$Be(s) + 1/2\ O_2(g) = BeO(s)$$



A. The whole laboratory as seen from the doorway

B. The hood facility and associated duct work (large box containing air filters may be seen in upper right)



C. Hood, recorders and programmer

D. Interior of hood containing furnace, balance and dessicator

Figure 2

PHOTOGRAPHS OF IITRI BERYLLIUM LABORATORY FACILITIES

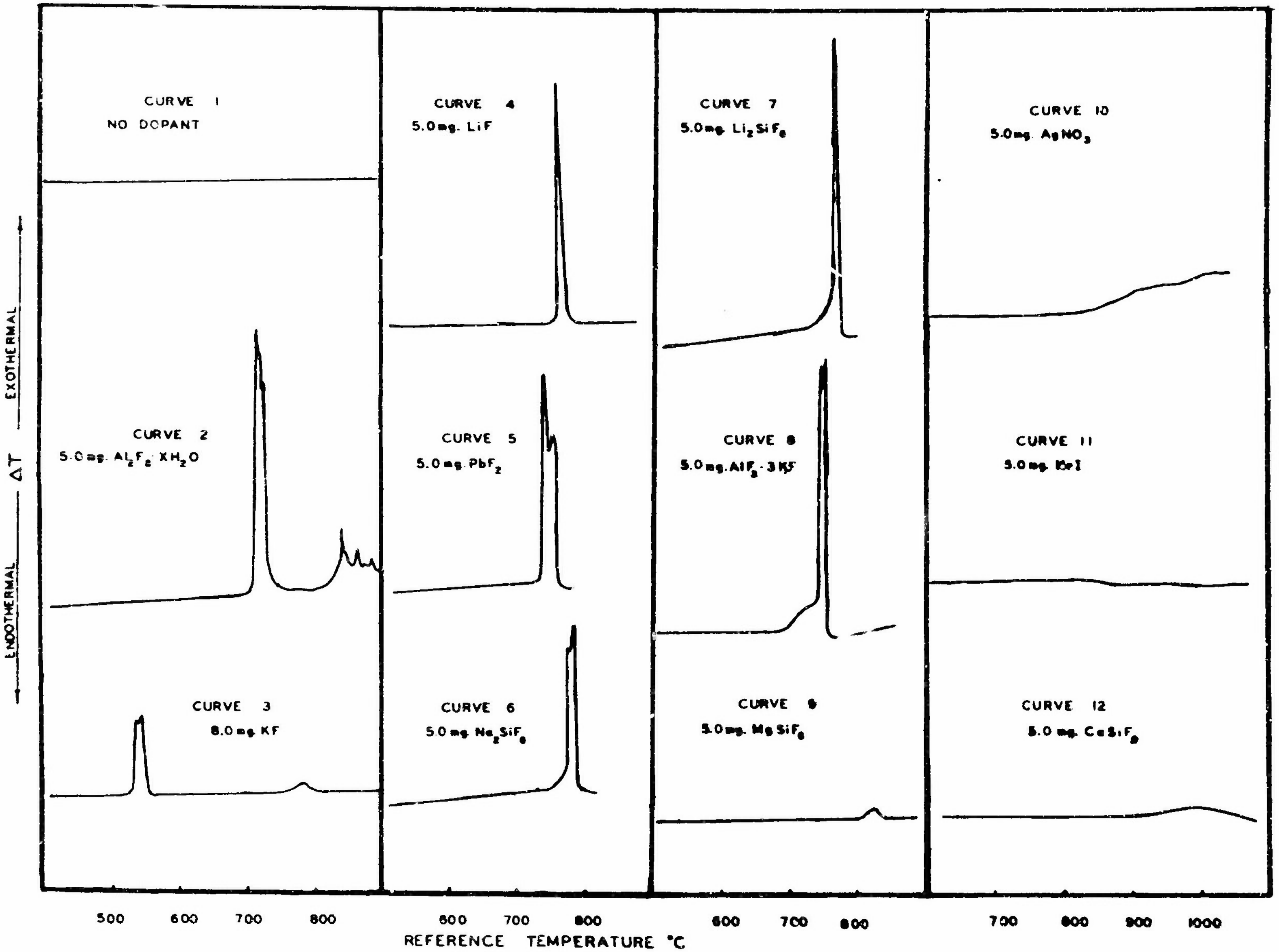


FIGURE 3

DIFFERENTIAL THERMAL ANALYSIS CURVES OF 75mg. OF DOPED AND UNDOPED BERYLLIUM. THE AMOUNT OF DOPANT USED IS SHOWN ON EACH CURVE. HEATING RATES ARE 10°C/MIN. OXYGEN FLOWS OF 300ML/MIN. WERE USED.

The absence of ignition was undoubtedly due to the formation of a protective oxide layer around the beryllium metal quenching the reaction. The latter phenomena has been observed and reported by several workers during their investigations on beryllium sheets.

Curve 2 (of Figure 3) shows the effects of doping by adding a small amount of $Al_2F_6 \cdot XH_2O$ to the powdered beryllium. It is evident the additive has markedly accelerated the reaction of beryllium with oxygen so that ignition took place at 700°C. Not only has ignition taken place but also the observed weight changes indicated that the combustion efficiency was doubled.

Many other dopants were found which caused the beryllium to ignite, however, the total increase in weight at the completion of reaction did not appear to be appreciably different from the undoped samples. It should be pointed out however, that the reason for this may have simply been due to the loss of the oxide from the open end of the reaction tube. Further experiments under more controlled conditions in which the oxide can be recovered should be conducted to determine the reaction efficiencies. There is little question, however, concerning the marked increase in the ignitibility of the beryllium due to doping.

Curves 3 through 12 show the differential thermal analysis of other beryllium-dopant mixtures. Table 2 summarizes the results of all the experiments performed on beryllium. Potassium fluoride has the most pronounced effect in lowering the ignition temperature of beryllium. The ignition temperature of the KF doped Be was 535°C. The ignition temperature of the aluminum fluoride doped sample was 700°C. The table shows the fluorosilicates of magnesium and calcium are the only ones of those investigated which have little effect on the rate of reaction between beryllium and oxygen.

LMH-2

The differential thermal analysis curve for LMH-2 in oxygen is shown in Curve 1 of Figure 4. Starting at approximately 300°C there appears to be a small endotherm with two overlapping peaks. This is followed by a sharp exotherm at 330°C. The sample weight was measured before and after this exotherm for the undoped sample and no appreciable change in sample weight was found to occur. Usually, endothermal or exothermal changes which are not accompanied by weight changes can be attributed to crystalline transitions or fusion. In this case, however, since hydrogen is so light it is possible that the DTA bands were accompanied by the loss of hydrogen. This is indicated by the observation that some water appeared to form around the top of the reaction vessel immediately after the exotherm at 330°C. This could be due to

Table 2

EFFECTS OF DOPING ON THE REACTIVITY OF BERYLLIUM

Wt. of Beryllium, 75 mg
Flow Rate of Oxygen, 300 ml/min
Heating Rate, 10°C/min

Dopant	Wt. of Dopant mg	Temperature (°C) of Peak of Exotherm(s) (From DTA Curves)	Minimum* Reaction Efficiency
None	None	No Peak Observed	.40±.10
$Al_2F_6 \cdot XH_2O$	5.0±2	700, 785, 820	.81±.10
KF	5.0±2	535	.40±.10
LiF	5.0±2	760	.30±.10
PbF_2	5.0±2	750	.30±.10
Na_2SiF_6	5.0±2	750	.30±.10
Li_2SiF_6	5.0±2	760	.25±.10
$AlF_3 \cdot 3KF$	5.0±2	760	.25±.10
$MgSiF_6$	5.0±2	No Peak Observed	.15±.10
$AgNO_3$	5.0±2	No Peak Observed	.30±.10
NaI	5.0±2	No Peak Observed	.10±.10
$CaSiF_6$	5.0±2	No Peak Observed	.25±.10

*Defined as the ratio of observed weight gain divided by the theoretical stoichiometric weight gain. Since oxide is rapidly lost from the reaction tube during ignition the value for efficiency is expected to be significantly higher.

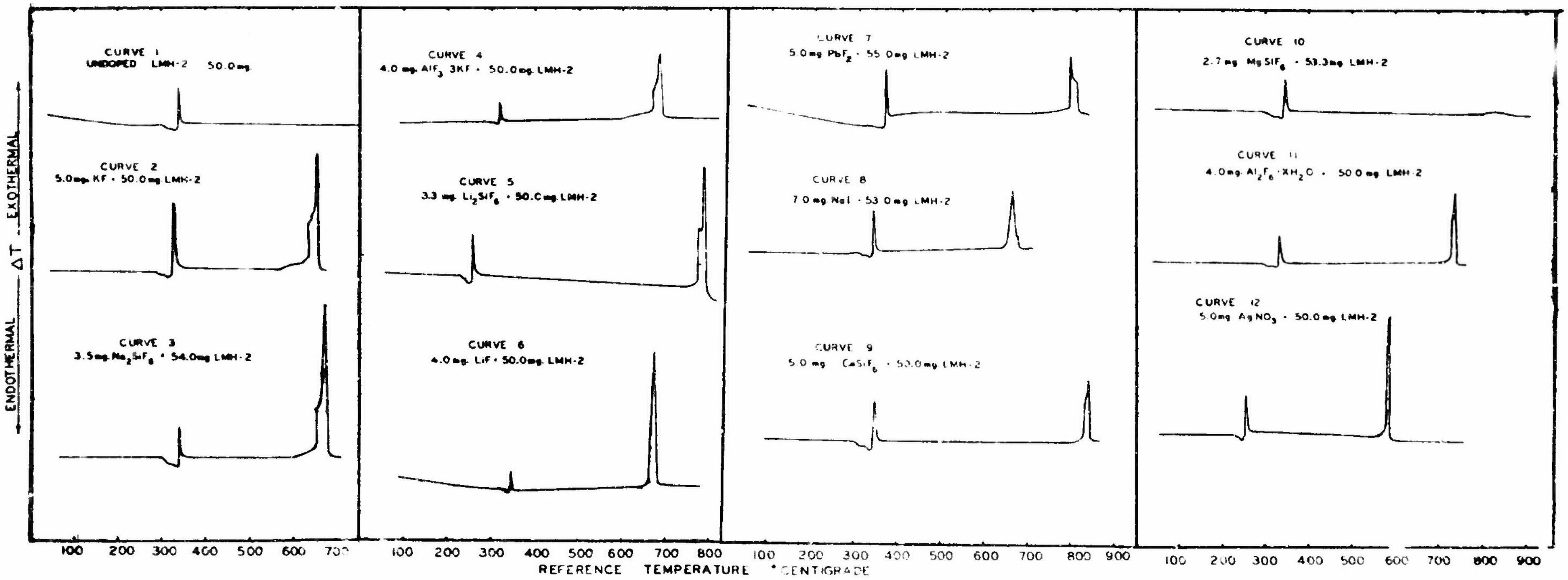


FIGURE 4

DIFFERENTIAL THERMAL ANALYSIS CURVES OF DOPED AND UNDOPED LMH-2
HEATING RATES ARE 10°C/MIN. OXYGEN FLOWS OF 300 ML/MIN. WERE USED

the reaction between hydrogen and the oxygen which was being admitted to the reaction tube. From 330°C to the end of the DTA run at about 1000°C, no additional exotherms or endotherms are observed and ignition did not occur. Ignition did occur, however, if the LMH-2 was doped.

Curves 2 to 12 in Figure 4 show the effects that doping has on the ignition of LMH-2 in pre-dried oxygen. It is clear that doping can markedly enhance the rate of oxidation and cause the system to ignite. Ignition of the LMH-2 occurs only in the doped systems and is evidenced by the sharp exotherm at temperatures of 600°C or higher depending on the doping impurity. Table 3 summarizes these results and also gives a measure of the combustion efficiency. It should be kept in mind, however, that the tabulated combustion efficiencies are minimum values since solid oxide is ejected out of the reaction tubes during the ignition of the doped samples. This does not occur in the case of the undoped samples which react slowly.

It can be concluded from Figure 4 that the most effect doping agent for LMH-2 in terms of lowest ignition temperature is $AgNO_3$. However, doping with the complex $AlF_3 \cdot 3KF$ seemed to result in highest minimum reaction efficiency of 0.81.

Ammonium Perchlorate

Figure 5 shows the results of differential thermal analysis experiments on doped and undoped ammonium perchlorate in argon. Curve 1 is the DTA curve for the undoped ammonium perchlorate. The first endotherm which starts at 240°C is due to the crystalline transition from the orthorhomic to cubic lattice. This is followed by two exotherms. The first occurs at 300°C and the second at 430°C. The thermal decomposition of ammonium perchlorate occurs in stages. The first exotherm represents the first or low temperature stage and the final high temperature stage of reaction is represented by the exotherm at 430°C. Although some work on these reactions has been done further studies are required to define these reactions.

Curves 2 and 8 show the effects of doping on the thermal decomposition of ammonium perchlorate. In Curve 2 KF is the dopant. The endotherm at 220°C is probably due to dehydration. This is followed by the endotherm for crystalline transitions and two large endotherms for thermal decomposition. The final exotherm peak occurs at 400°C rather than 430°C as in the case of the undoped sample. Table 4 summarizes the results.

This series of curves illustrates the strong influence a small amount of dopant exerts on the DTA curve of NH_4ClO_4. Most of the doping agents lowered the temperature of major decomposition of the perchlorate to some degree. The two exceptions were KF and $Al_3 \cdot 3KF$.

Table 3

SUMMARY OF RESULTS OF DTA EXPERIMENTS ON LMH-2

Weight of LMH-2, 50-54 mg
Flow Rate of Oxygen, 300 ml/min
Heating Rate, 10°C/min

Dopant	Wt. of Dopant (mg)	Temperature (°C) of Peak of Exotherm (s) (From DTA Curves)	Minimum* Reaction Efficiency
None	None	No Ignition Peak	.80±.10
KF	5±2	650	.60±.10
Na_2SiF_6	5±2	670	.80±.10
$AlF_3 \cdot 3KF$	5±2	680	.80±.10
Li_2SiF_6	5±2	785	.75±.10
LiF	5±2	670	.65±.10
PbF_2	5±2	792	.80±.10
NaI	5±2	660	.65±.10
$CaSiF_6$	5±2	840	.80±.10
$MgSiF_6$	5±2	No Ignition Peak	.80±.10
$Al_2F_6 \cdot XH_2O$	5±2	730	.65±.10
$AgNO_3$	5±2	585	.65±.10

*Defined as the ratio of observed weight gain divided by the theoretical stoichiometric weight gain. These values are a minimum since oxide is expelled from the reaction tube during ignition.

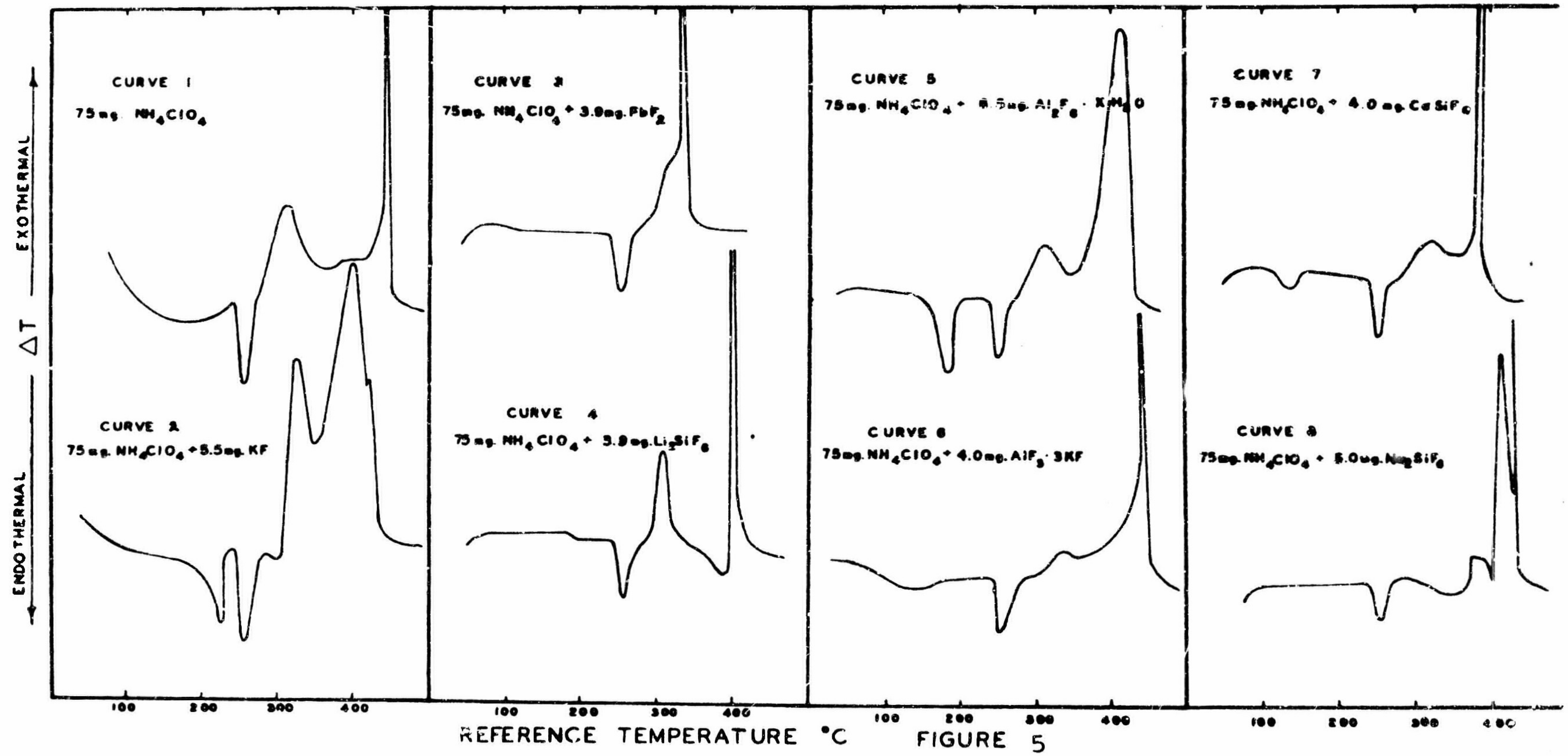


FIGURE 5

DIFFERENTIAL THERMAL ANALYSIS CURVES OF DOPED NH_4ClO_4.
SIEVE FRACTION, 100/120 - HEATING RATE, 10°C/MIN. - ATMOSPHERE, ARGON FLOW OF 300ML/MIN. - PRESSURE, 1 ATM.

Table 4

SUMMARY OF RESULTS OF THE DTA CURVES OF DOPED AMMONIUM PERCHLORATE

Dopant	% Dopant	# of Peaks	Type of Peaks	Peak Temperature °C	Phenomena
None	None	3	1 endotherm 2 exotherms	255 310; 445	Crystalline transitions decomposition dehydration
Doping Study					
KF	5 ± 2	4	2 endotherms 2 exotherms	440; 255 325; 445	Crystalline transitions decomposition dehydration
$Al_2F_6 \cdot XH_2O$	5 ± 2	4	2 Endotherms 2 exotherms	188; 253 310; 420	Crystalline transitions decomposition dehydration
$AlF_3 \cdot 3KF$	5 ± 2	3	1 endotherm 2 exotherms	255 320; 445	Crystalline transitions decomposition dehydration
PbF_2	5 ± 2	2	1 endotherm 1 exotherm	253 338	Crystalline transitions decomposition dehydration
Li_2SiF_6	5 ± 2	4	2 endotherms 2 exotherms	253; 388 305; 400	Crystalline transitions decomposition dehydration
$CaSiF_6$	5 ± 2	4	2 endotherms 2 exotherms	140; 253 325; 385	Crystalline transitions decomposition dehydration
Na_2SiF_6	5 ± 2	4	1 endotherm 3 exotherms	253 378; 418; 433	Crystalline transitions decomposition dehydration

Table 4 (Cont.)

SUMMARY OF RESULTS OF THE DTA CURVES OF DOPED AMMONIUM PERCHLORATE

Dopant	% Dopant	# of Peaks	Type of Peaks	Peak Temperature °C	Phenomena
1:1 Mixture Study					
KF	50	8	7 endotherms	100; 120; 205; 230; 310; 510; 520	Due to chemical reactions and/or dehydrati
			1 exotherm	605	Chemical reaction
$Al_2F_6 \cdot XH_2O$	50	4	2 endotherms	205; 253	Chemical reaction and/ or dehydration
			2 exotherms	320; 370	Chemical reaction
$AlF_3 \cdot 3KF$	50	6	4 endotherms	120; 253; 310; 510	Chemical reaction and/ or dehydration
			2 exotherms	418; 550	Chemical reaction
PbF_2	50	5	3 endotherms	253; 332; 359	Chemical reaction and/ or dehydration
			2 exotherms	397; 410	Chemical reaction
Na_2SiF_6	50	7	6 endotherms	255; 430; 440; 445 458; 702	Chemical reaction and/ or dehydration
			1 exotherm	557	Chemical reaction
Li_2SiF_6	50	6	4 endotherms	250; 328; 402; 480	Chemical reaction and/ or dehydration
			2 exotherms	420; 511	Chemical reaction
$CaSiF_6$	50	4	3 endotherms	151; 253; 305	Chemical reaction and/ or dehydration
			1 exotherm	375	Chemical reaction

Two important observations concerning the doped mixtures may be made.

1. The temperature at which the major decomposition exotherm of NH_4ClO_4 appears (normally observed at 445°C) was reduced by more than 100°C in the presence of 5 weight percent PbF_2.

2. $Al_2F_6 \cdot XH_2O$, Li_2SiF_6, $CaSiF_6$ and Na_2SiF_6 to a lesser extent reduced the temperature at which exothermal decomposition of NH_4ClO_4 took place.

1:1 Mixtures (Figure 6)

In using the 1:1 mixtures it was necessary to differentiate between DTA peaks solely attributable to the doping agent and those attributable to chemical and other effects of the agent on NH_4ClO_4. None of the dopants exhibited DTA exotherms, but endotherms due to dehydration or decomposition were observed. The following dopants exhibited dehydration endotherms: $Al_2F_6 \cdot XH_2O$ (188-220°C), $CaSiF_6$ (140-150°C), KF (100-120°C, $AlF_3 \cdot 3KF$ (120°C). Agents which exhibited decomposition endotherms include Na_2SiF6 (485°C), $CaSiF_6$ (230-255°C) and Li_2SiF_6 (370-380°C).

In most cases, where doping materials were added to ammonium perchlorate, the first order phase transition (NH_4ClO_4, orthorhombic to NH_4ClO_4, cubic) has a peak at 255°C and is consistently present. It can be concluded that these agents have no effect on NH_4ClO_4 below 240°C.

A notable exception is observed in the case of KF. At least one of the endotherms observed in the DTA spectrum of the 1:1 mixture of NH_4ClO_4 and KF is indicative of a chemical reaction and the crystalline transition of NH_4ClO_4 normally seen as an endotherm at 240°C is not present. The weight change associated with the DTA experiment is anomalous, (Table 5) since only 65% of the normal weight loss is observed. Apparently KF reacts directly with NH_4ClO_4 to form a nonvolatile compound.

Freeman[7] has observed PbF_2 to be stable below 700°C (no DTA peaks occur below 700°C). The DTA curves of NH_4ClO_4-PbF_2 mixtures (1:1) indicate PbF_2 either decomposes in the presence of, or enters into direct reaction with NH_4ClO_4. The endotherm observed between the crystalline phase transition and the decomposition exotherm of NH_4ClO_4 (between 244 and 410°C) suggests chemical reaction. The anomalous weight loss associated with the DTA curve (Table 5) suggests decomposition. The need for further work is indicated.

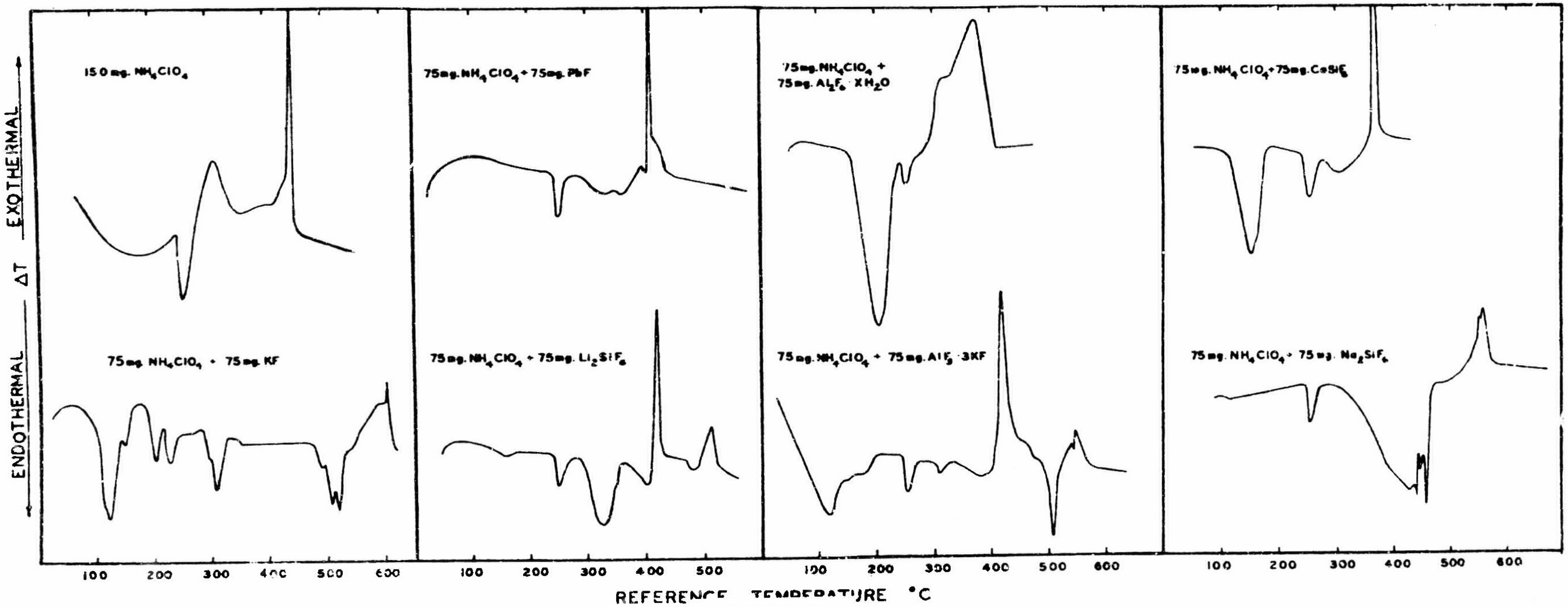


FIGURE 6

DIFFERENTIAL THERMAL ANALYSIS CURVES OF 1:1 RATIO NH_4ClO_4 AND DOPANT HEATED AT 10°C/MIN. IN AN ARGON FLOW OF 300ML/MIN. AT A PRESSURE OF 1 ATMOSPHERE.

Table 5

WEIGHT CHANGES ASSOCIATED WITH THE DTA CURVES OF DOPED NH_4ClO_4

Doping Agent	Weight of NH_4ClO_4, mg	Weight of Dopant, mg	Net Weight Loss After Reaction, mg
None	75.0	None	75
KF	150.00	7.5	104
PbF_2	75.0	75.0	93.3
PbF_2	75.0	3.9	78.0
Na_2SiF_6*	75.0	75.0	118.0
$CaSiF_6$*	75.0	76.0	130.2

* These two compounds undergo the following decomposition reactions:

$$Na_2SiF_6 \longrightarrow 2NaF_{(solid)} + SiF_4\ (gas)$$

$$CaSiF_6 \longrightarrow CaF_{2(solid)} + SiF_4\ (gas)$$

Also see discussion in text

Effects of Water Vapor

Beryllium

Experiments were conducted to probe the effect that water vapor may have on the combustion of beryllium in oxygen. Figure 7 shows the results of the differential thermal analysis experiments. It may be seen that in the presence of moisture the undoped beryllium will undergo sufficiently rapid combustion in oxygen to exhibit a definite exotherm ranging from approximately 810°C to 910°C. It may be recalled that there was no exotherm observed to occur in pre-dried oxygen over the same temperature range. This indicates that water has an accelerative effect on the oxidation reaction. The mechanism is not known but it is apparently catalytic in nature.

Curve 2 shows that if the Be is doped, in this case with $Al_2F_6 \cdot XH_2O$, the combustion reaction is considerably more rapid and that the ignition temperature is lowered approximately 185°C, from 910°C to 725°C.

LMH-2

Curve 3 shows the DTA curve for the combustion of undoped LMH-2 in oxygen in the presence of water vapor. As was seen in the case of Be, the water vapor appears to catalyze the combustion process as is indicated by the exotherm at approximately 675°C. Again, however, it is seen that by doping with KF the combustion is significantly more rapid as indicated by the height and sharpness of the exotherm. Here the ignition temperature did not seem to be altered appreciably.

Compositions Containing Ammonium Perchlorate

Figure 8 shows the results of differential thermal analysis experiments which were carried out on binary systems of ammonium perchlorate and fuel.

The results indicate that the beryllium and LMH-2 catalyze the decomposition of ammonium perchlorate. The sharpness of the exotherm also indicates that some oxidation of the metal fuel may have also occurred. LiF appears to have a more pronounced effect in increasing the reactivity of the beryllium system than KF. The effects of the dopants are clearly not only due to their effects on ammonium perchlorate as can be seen by comparisons with the curves for ammonium perchlorate in the absence of the fuels.

In the case of LMH-2 it appears that the primary effect of the dopant is similar to the effect it has on LMH-2 in the absence of the ammonium perchlorate. Again it is seen that $AgNO_3$ has the largest effect in reducing the temperature of the initial exotherm by 80°C.

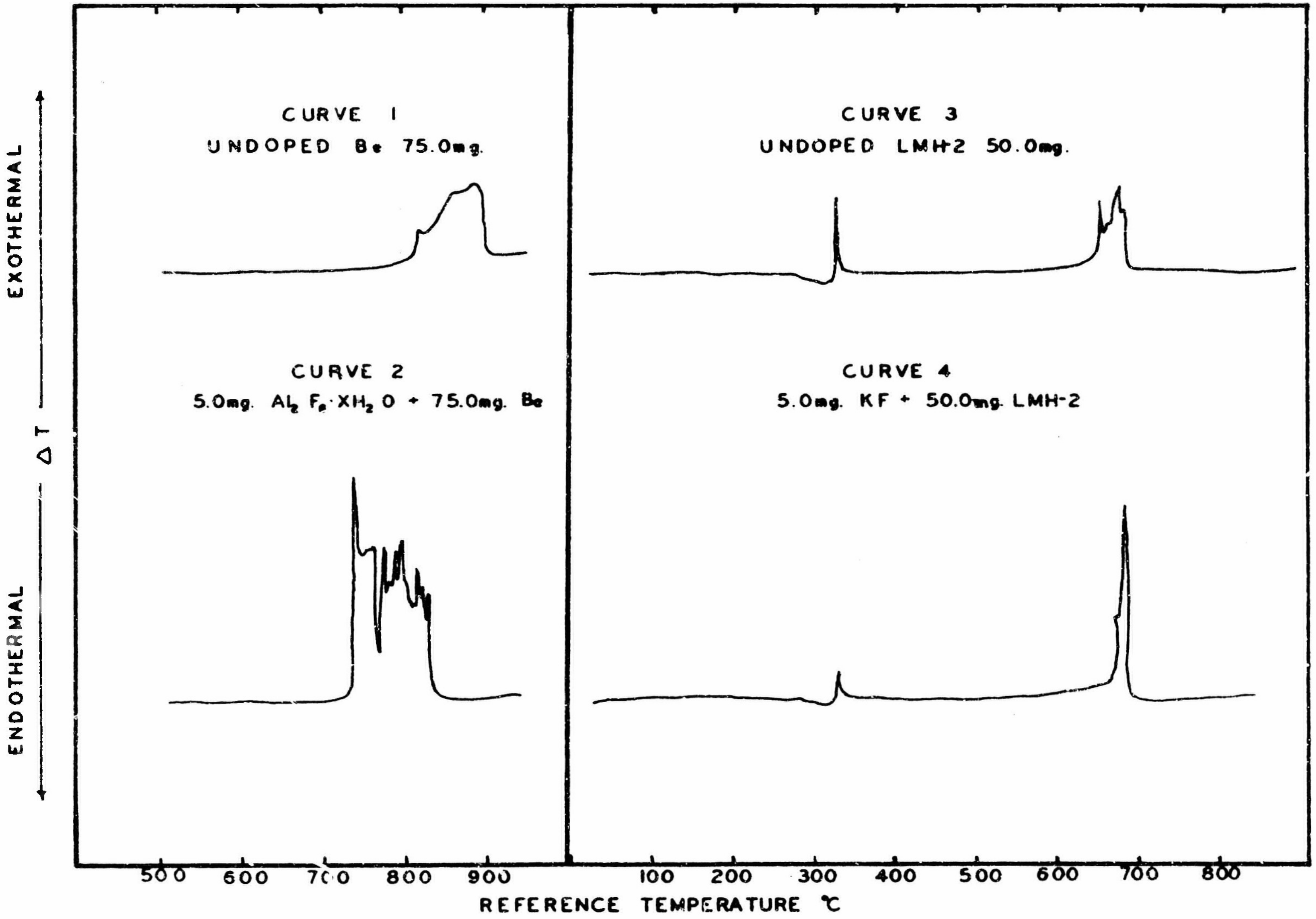


FIGURE 7

DIFFERENTIAL THERMAL ANALYSIS OF DOPED AND UNDOPED Be
HEATING RATES ARE: 10°C/MIN. OXYGEN SATURATED WITH
WATER VAPOR USED. FLOW RATE: 300 ML/MIN

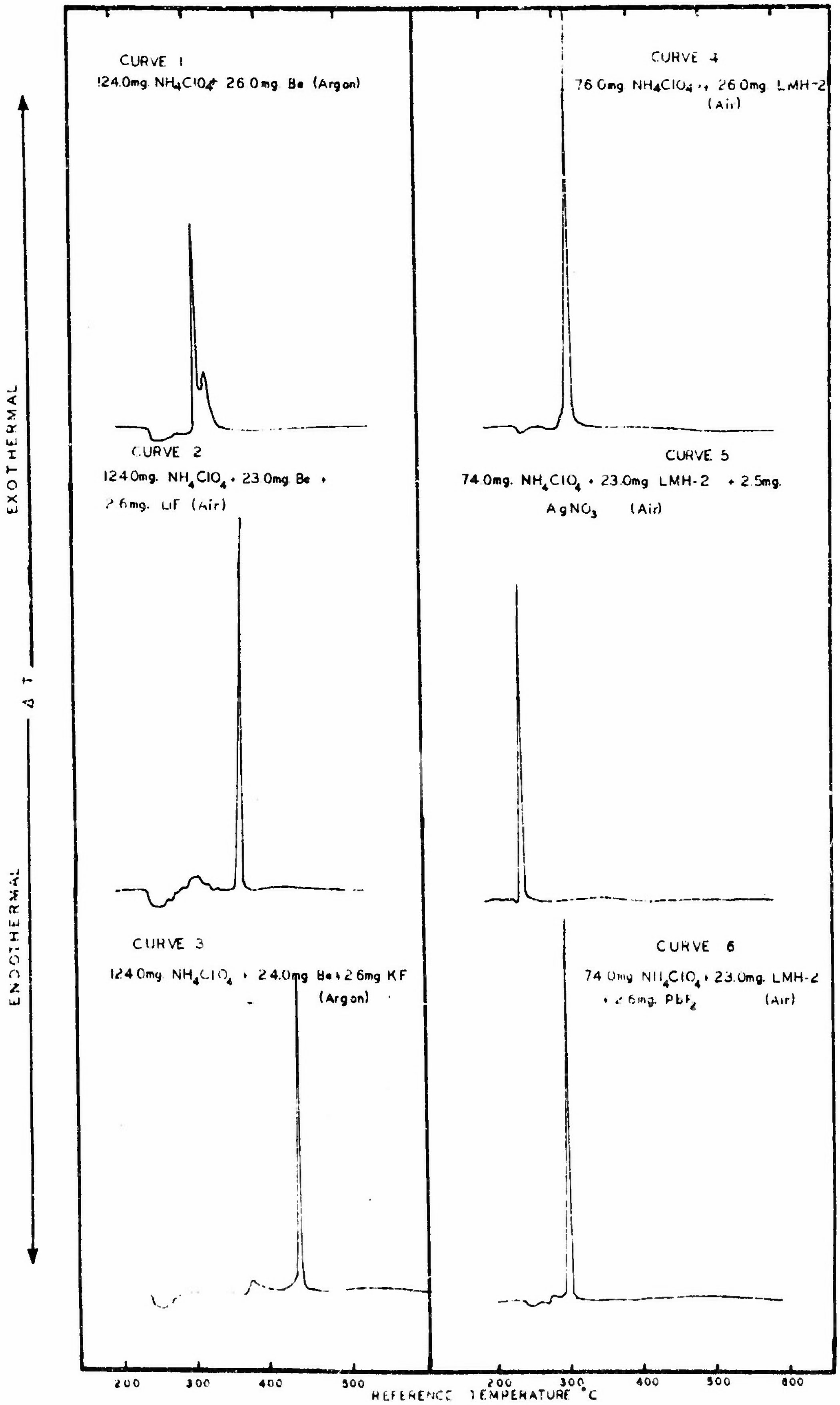


FIGURE 8

DIFFERENTIAL THERMAL ANALYSIS CURVES OF BINARY MIXTURES OF NH$_4$ClO$_4$ AND DOPED AND UNDOPED BERYLLIUM AND LMH-2. HEATING RATE: 10°C/MIN

SECTION III

SUMMARY

1. Doping with selected impurities including silver nitrate, various metal fluorides and silicofluorides can significantly increase the chemical reactivity of beryllium and LMH-2 fuels in oxygen. The doped fuels appear to undergo self-propagative combustion.

2. Water vapor accelerates the rate of oxidation of both beryllium and LMH-2 in oxygen.

3. Doping accelerates the thermal decomposition of ammonium perchlorate and affects the reactions of beryllium and LMH-2 in the presence of ammonium perchlorate.

SECTION IV

RECOMMENDATIONS

This present program has strongly indicated the feasibility of increasing the reactivity and rate of combustion of Be and LMH-2 fuels. For this reason it is recommended that the next step be taken, which is to conduct the required follow on research program, so that a new doped fuel system may be developed with improved burning and combustion characteristics.

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APPENDIX

Figures 1 and 2 show the effects of doping on the chemical reactivity of LMH-2 powders. Figure 1 shows the results of the control experiments in which the LMH-2 powder is not doped. No ignition occurred when the sample was heated from room temperature to 900°C in a flow of pre-dried oxygen. Under the same experimental conditions the LMH-2 powder ignited at approximately 700°C as is shown in Figure 2. The glow due to the ignition of the powder is seen in the figure. In this case the sample was doped with lithium fluoride.

Figure 1

Undoped LMH-2 in a differential thermal analysis experiment heated at 10°C/min from 25°C to 900°C in pre-dried oxygen at a flow rate of 300 ml/min.

Figure 2

LMH-2 powder doped with lithium fluoride in a differential thermal analysis equipment heated at 10°C/min from 25°C to 900°C in pre-dried oxygen at a flow rate of 300 ml/min.

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13. ABSTRACT

The effects of doping on the chemical reactivity of beryllium and LMH-2 with respect to combustion was studied by means of differential thermal analysis (DTA). Specifically, the effects on doping with impurities on combustion was explored to determine if it is possible to increase the ignitibility of the fuels of interest. It was found that when beryllium and LMH-2 were heated under conditions of linearly increasing temperature from room temperature to 800°C in dry oxygen ignition did not take place. Under the same experimental conditions ignition occurred when the materials were doped with various metal fluorides or fluoro-silicates. The ignition temperature varied depending on the dopant impurity used.

When an oxygen atmosphere saturated with water vapor in place of dry gas was used the reactivity of both fuels increased markedly. The exothermal decomposition of ammonium perchlorate was also observed to be catalyzed by some fluoride additives. Mixtures composed of the doped and undoped fuels and ammonium perchlorate were also investigated.

14. KEYWORDS

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