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NH_4ClO_4 Decomposition with Nitrates of La, Ce, Nd, Sm, Eu

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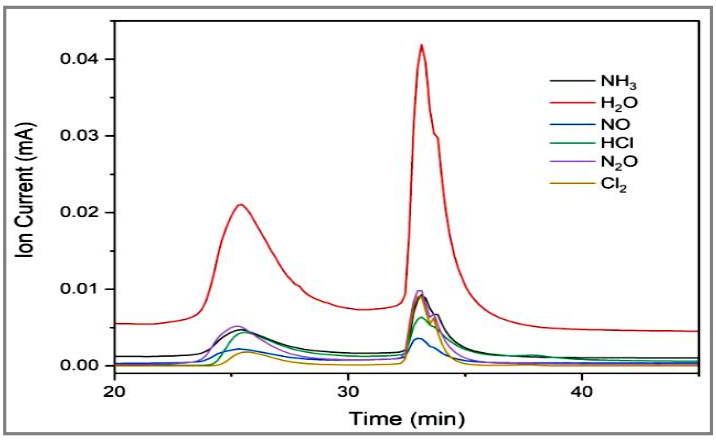
ABSTRACT

Thermal decomposition of ammonium per chlorate in the presence of lanthanide (Ln) nitrates, where Ln = La, Ce, Nd, Sm, and Eu is studied. The analytical techniques of mass spectrometry (MS), thermo gravimetric (TG), and differential Scanning Calorimetry (DSC) have been employed. In all the cases of Ammonium Per chlorate (AP)-Lanthanide nitrate mixtures, the major product evolved is H_2O.Besides H_2O, HCl, and NH_3 are common products released. N_2O, Cl_2, and O_2 have not been observed in the case of pure AP. In the case of AP-Samarium nitrate system NO is not observed, and $O_2$is the other major product evolved. The cessation of decomposition of AP after an initial conversion of 30 percent is modified in the presence of nitrates of La, Nd, Sm, and Eu in the range between 35 % and 50%. In terms of heat release, Samarium nitrate gives better energy output (1207 J g^{-1}).

Graphical Abstract



TG-MS peaks corresponding to pure AP-Neodymium Nitrate.

Keywords: Ammonium, per chlorate, lanthanide nitrates, MS, TGA, DSC.

INTRODUCTION

Wendlandt [1] has shown that the rare-earth nitrates, with the exception of cerium and samarium, decompose according to the general reaction:

$$M(NO_3)_3.\ 6\ H_2O(s) \longrightarrow M\ (NO_3)_3(s) \longrightarrow MONO_3(s) \longrightarrow \text{metal oxide}$$

Thermal decomposition of anhydrous cerium nitrate differs from that of Neodymium nitrate [2]. Thermal decomposition of neodymium (III) nitrate has been reinvestigated by Vuuren *et al* [3]. Thermal decomposition of several metal nitrates and nitrites, particularly those of rare earths has been investigated through IR spectroscopy to study the nature of the intermediates in their decomposition [4]. Arora *et al* [5] studied Lanthanide (III) nitrate complexes of Schiff base ligands.

Several $M^{III}(NO_3)_4^-$ were produced by electro spray ionization and subjected to low energy collision induced dissociation in quadrupole ion trap mass spectrometer; and the nature of the $MO(NO_3)_3^-$ products that result from NO_2 elimination was experimentally evaluated by their hydrolysis to produce $M^{III}(OH)(NO_3)_3^-$ [6]. The thermal decomposition kinetics of some anhydrous lanthanide nitrates were investigated and compared with those of neodymium nitrate [7]. Strydom [8] studied the thermal decomposition reactions of some lanthanide and uranium (IV) nitrates. Thermal decomposition kinetics of gadolinium (III), holmium (III), and erbium (III) nitrates was studied by Strydom *et al* [9].

Peter *et al* [10] studied the thermal decomposition of praseodymium nitrate hexahydrate. Bamidele *et al* [11] studied non-isothermal kinetics and mechanistic aspects of thermal decomposition of light rare earth metal nitrate hydrates through thermo-analytical techniques.Mentus *et al* [12] reported the decomposition of lanthanum nitrate by both temperature programmed heating and citrate gel combustion.

The focus in the present study is to understand the role played by the nitrates of Lanthanum, Cerium, Neodymium, Samarium, and Europium in the thermal decomposition of ammonium per chlorate, an inorganic crystalline oxidizer widely used in composite solid rocket propellant technology.

MATERIALS AND METHODS

The ammonium per chlorate (AP) employed in this study was procured from Vikram Sarabhai Space Centre (VSSC), Indian Space Research Organization (ISRO), Department of Space(DOS), Government of India. Samarium (III) Nitrate hexahydrate, Europium (III) Nitrate hexahydrate, Neodymium (III) Nitrate hexahydrate were procured from Sigma Aldrich. Cerium Nitrate and Lanthanum (III) Nitrate hexahydrate were procured from S. D. Fine Chemicals Ltd.

The thermal decomposition studies were carried out employing a sample mass of 5 mg; inert gas (N_2) flow-rate of 50 mL min^{-1}, and a sample heating rate of 10°C min^{-1} were maintained. Experiments were carried out in two instruments TA Instruments - Model SDT Q600 TD System, and Model SDT DSC 250.

RESULTS AND DISCUSSION

The thermo gravimetric (TG) curves for pure AP and, AP mixtures with the nitrates of Lanthanum (AP-LaN), Cerium (AP-CeN), Neodymium (AP-NdN), Samarium (AP-SmN), and Europium (AP-EuN) are presented in figure 1. The temperature intervals of low-temperature decomposition (LTD), and high-temperature decomposition (HTD); and the percentage decomposition of the material during

LTD and HTD; the residual content in each case are presented in table 1. The residues observed are basically the corresponding metal oxides.

The temperatures of onset and end set of decomposition for these mixtures are presented in table 2. Except for Cerium nitrate and Europium nitrate, for the rest of the mixtures, the onset temperatures of decomposition are of the same order of magnitude. From the end set of decomposition point of view, the order of temperature is AP – EuN< AP – NdN< AP – SmN< AP – LaN< AP – CeN. It is a well known fact that, AP decomposition ceases at 30%. However, as we move from AP-Lanthanum Nitrate system to AP-Europium Nitrate system (Table 1), we notice that, the low-temperature decomposition (LTD) does not cease at 30 percent but progresses to a higher extent up to 50.5 percent as in the case of AP-Europium Nitrate system.

Table 1. Thermal decomposition data of mixtures of AP with Nitrates of La (LaN), Ce (CeN), Nd (NdN), Sm (SmN),Eu (EuN)and pure AP

AP-Lanthanide Nitrate Mixture	Low-temperature Decomposition (LTD)		High-temperature Decomposition (HTD)		Residue (%)
	Temperature Interval (°C)	Decomp. (%)	Temperature Interval (°C)	Decomp. (%)	
Pure AP	249.5 - 329	29.1	331.3 - 452.0	70.9	0.0
AP – CeN	205.8 - 302	30.8	305.2 - 425.3	66.0	3.2
AP – LaN	223.7 - 310.2	35.3	313.3 - 419.2	59.6	5.1
AP – NdN	222.5 - 306.5	39.3	307.6 - 406.6	56.3	4.4
AP – SmN	220.8 - 301.2	40.7	304.3 - 409.9	54.3	5.0
AP – EuN	212.8 - 312.4	50.5	315.1 - 397.0	44.4	5.1

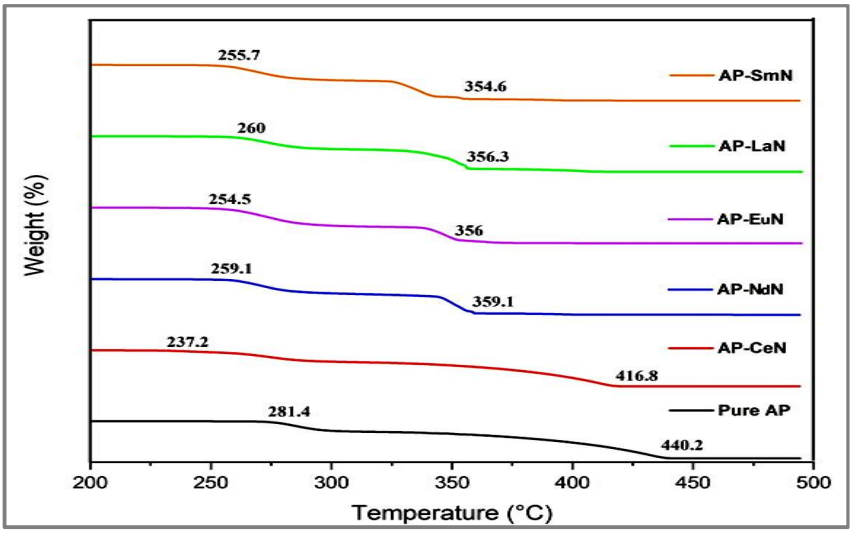


Figure 1. TG-DTG Curves of pure AP and mixtures of AP with nitrates of Sm, La, Eu, Nd, and Ce

Table 2. Onset and end set of temperatures of decomposition of pure AP and its mixtures with nitrates of La (LaN), Ce (CeN), Nd (NdN), Sm (SmN), and Eu (EuN)

Mixture Designation	Temp. of onset of decomposition (^{o} C)	Temp. of end set of decomposition (^{o} C)	Temperature Interval (^{o} C)
AP	281.4	440.2	158.8
AP – LaN	223.7	419.2	195.5
AP – NdN	222.5	406.6	184.1
AP – SmN	220.8	409.9	189.1
AP – EuN	212.8	397.0	184.2
AP – CeN	205.8	425.3	219.5

The differential scanning calorimetric (DSC) curves of pure AP and mixtures of AP with nitrates of Lanthanum, Cerium, Neodymium, Samarium, and Europium are presented in figure 2. The enthalpy changes for the endothermic crystallographic phase-transition of pure AP in the presence of nitrates of La, Ce, Nd, Sm, and Eu are presented in table 3.

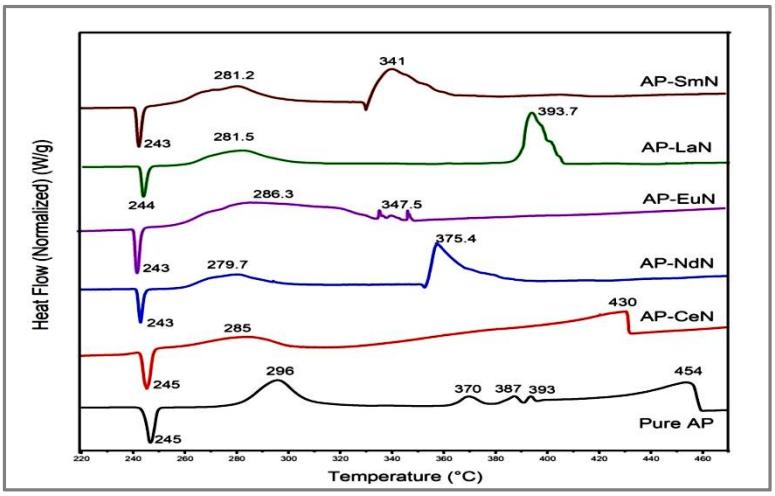


Figure 2. DSC Curves of pure Ammonium per chlorate (AP), and Its Mixtures with Nitrates of La, Ce, Nd, Sm, and Eu.

Table 3. Enthalpies of Crystallographic Phase-transition of Pure AP and its mixtures with nitrates of La, Ce, Nd, Sm, and Eu

Sample System	Phase-transition Temperature	Enthalpy (J. g^{-1})
AP	245.1	85.2
AP – NdN	243.1	69.8
AP – CeN	245.5	73.5
AP – SmN	243.4	81.4
AP – LaN	243.6	86.9
AP – EuN	243.2	93.4

From table 3 it can inferred that, there is no appreciable change in the crystallographic phase-transition of AP in the presence of nitrates of La, Ce, Nd, Sm, and Eu. Except in the case of nitrates of Neodymium and Cerium nitrate where the enthalpy is decreased; the enthalpy in the case of Europium nitrate, it is increased. However, in the presence of Lanthanum and Samarium nitrates, the enthalpy of AP is not affected appreciably. The temperatures of maximum rate of decomposition in the low-temperature regime and high-temperature regime of pure AP and, AP in the presence of nitrates of La, Ce, Nd, Sm, and Eu; and the corresponding enthalpy changes are presented in table 4.

Table 4. Kinetic data of thermal decomposition of pure AP and Its mixtures with nitrates of La, Ce, Nd, Sm, and Eu

Sample System	Temp. of maximum rate of Decomp. (°C)		Enthalpies of Exothermic Decomp. ($J.g^{-1}$)		Total Enthalpy of Exothermic Decomp. (J. g^{-1})
	Low-Temp. Decom. (LTD)	High-temp. Decom. (HTD)	Low-temp. Decom. (LTD)	High-temp. Decom. (HTD)	
AP	300.0	461.0	326.0	302.6	628.6
AP–LaN	281.5	393.7	436.2	588.4	1024.6
AP – CeN	285.0	430.1	175.0	652.4	827.4
AP–NdN	279.7	357.4	320.4	602.6	923.0
AP – SmN	281.2	340.9	463.4	743.5	1207.0
AP – EuN	279.7	357.4	320.4	602.6	923.0

From the total enthalpy consideration, AP-Samarium Nitrate and AP-Lanthanum Nitrate systems proved to be more effective in modifying the thermal decomposition of AP. AP-Neodymium Nitrate and AP-Europium Nitrate systems give the same enthalpy release in the order of next preference. The total enthalpy release with respect to AP- Cerium nitrate system is relatively least. However, all the catalysts yield more enthalpy than pure AP. The TG-MS curves for these systems are presented in figure 3 to figure 8.

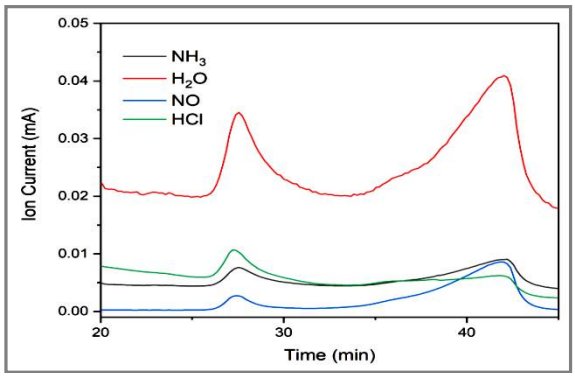


Figure 3. TG-MS peaks corresponding to pure AP

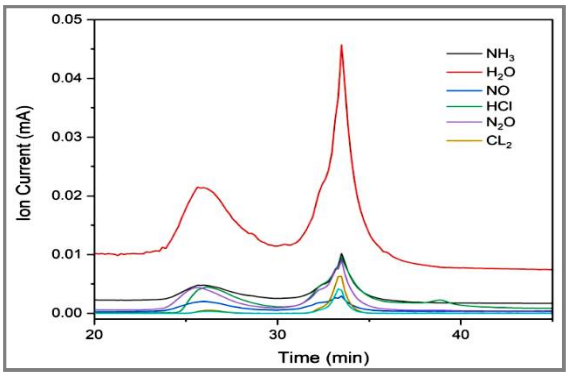


Figure 4. TG-MS peaks corresponding to pure AP-Lanthanum Nitrate system.

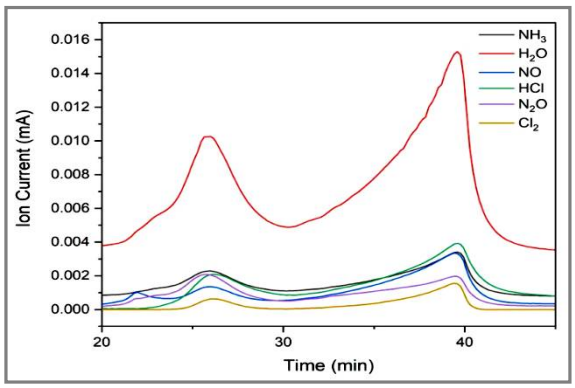


Figure 5. TG-MS peaks corresponding to pure AP-Cerium Nitrate system.

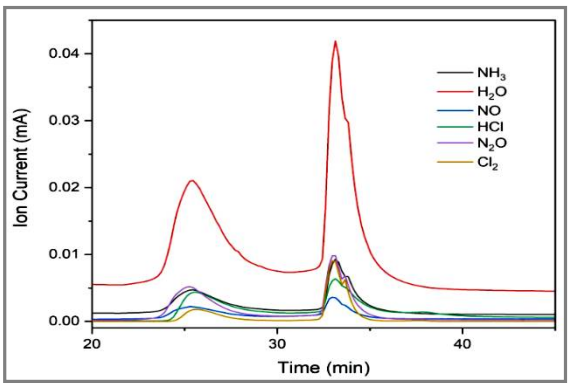


Figure 6. TG-MS peaks corresponding to pure AP-Neodymium Nitrate.

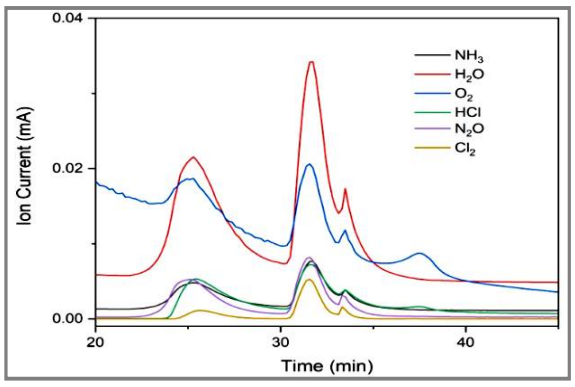


Figure 7. TG-MS peaks corresponding to pure AP-Samarium Nitrate.

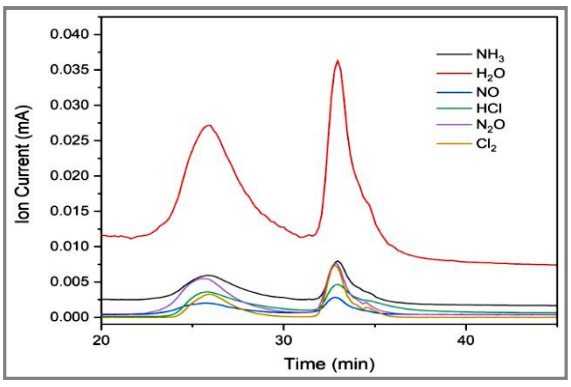


Figure 8. TG-MS peaks corresponding to pure AP-Europium Nitrate.

Table 5. The summary of the data from figure 3 to 8

Sample System	Decomposition Species Observed						
	H_2O	HCl	NH_3	NO	N_2O	Cl_2	O_2
Pure AP	✓	✓	✓	✓	x	x	x
AP – LaNi	✓	✓	✓	✓	✓	✓	x
AP – CeN	✓	✓	✓	✓	✓	✓	x
AP – NdN	✓	✓	✓	✓	✓	✓	x
AP – SmN	✓	✓	✓	x	✓	✓	✓
AP – EuN	✓	✓	✓	✓	✓	✓	x

In all the cases H_2O is the major product evolved during decomposition. H_2O, HCl, and NH_3 are the common products released in all the cases studied. N_2O, Cl_2, and O_2 have not been observed in the case of pure AP. In the case of AP-Samarium nitrate system (NO) is not observed, and the second major product evolved is O_2.

APPLICATION

This data is useful in modifying the decomposition of AP, which in turn modifies the combustion performance of AP-based composite solid rocket propellants

CONCLUSION

Samariuam Nitrate is the best among all the lanthanide nitrates studied towards improving AP thermal decomposition.

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