

ALH₃-BASED SOLID PROPELLANT DEVELOPMENT AND CHARACTERIZATION IN GRAIL H2020 PROJECT

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ABSTRACT

The use of aluminum hydride (AlH₃, alane) has always been addressed by the competent literature as an important target for chemical propulsion development. The availability of such material impairs its use. Several attempts were made in the past to develop stable and pure alane crystals. The sensitivity of the final result from the production process makes this task quite complex. This paper presents the current development status of aluminum hydride production and characterization in the frame of GRAIL (Green Advanced High Energy Propellants for Launchers) project, financed in the frame of the Horizon 2020 initiative. Morphology, calorimetry, and crystallography are used to identify the behavior of fresh and aged aluminum hydride.

1. INTRODUCTION

Metal hydrides in solid rocket propulsion are attractive fuels from the theoretical viewpoint due to the capability of incrementing the gravimetric. These materials can be considered as solid hydrogen carriers with improved storage capability, if compared to cryogenic cylinders [1]. Under specific conditions, these molecules can undergo both reversible and irreversible hydrogen release, paving the way to several industrial applications, including development of new tank concepts, hydrogen generation for fuel cells, or combustion uses [2,3].

Solid rocket motors are featured by a relatively low specific impulse, out of the thermochemical propulsion family. If a monophasic mixture is considered, the ideal specific impulse is dependent upon the properties in combustion chamber, and specifically to $\sqrt{T_f/M_{mol}}$, under the hypothesis of frozen expansion model and calorically perfect gas [4]. Thermochemical computations have shown that the use of a metal hydride in a solid propellant formulation does not lead to improvements in adiabatic flame temperature, rather, the molar mass decreases. The combustion process is oxidizer-lean so part of the hydrogen released by the decomposition of the original molecule does not react and acts as a diluting agent. Moreover, the equilibrium of oxidation is influenced by the presence of more oxygen-demanding species. Part of molecular hydrogen is unreacted reducing the mean molecular mass of the mixture. On the other hand, enthalpy of combustion is not released. The representation of such a behavior is reported in Figure 1. Equilibrium computations for adiabatic flame temperature and molar masses are reported for a propellant based on ammonium perchlorate (AP), inert binder, and variable blend of aluminum and its hydride. The baseline formulation is AP/Al/inert binder having mass ratio 68/18/14. NASA CEA code was used [5].

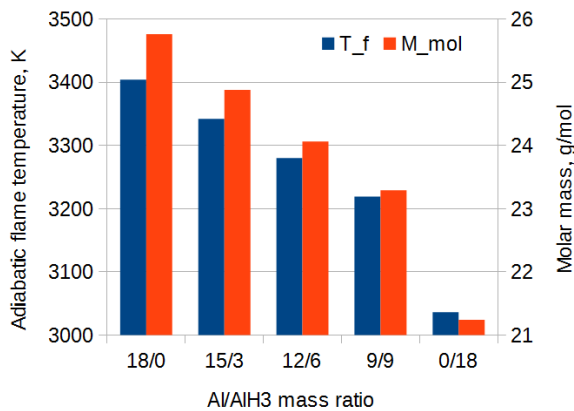


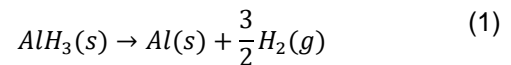
Figure 1 Equilibrium computations for replacement of Al with AlH₃. Original formulation AP/Al/binder having mass ratio 68/18/14 at 70 bar

The replacement of metallic aluminum with a metal hydride may lead to some penalties due to their limited specific gravity. A systematic comparison in solid and hybrid rocket motor performance was published by the SPLab research group. The study highlighted that both I_s and I_v are incremented only when aluminum hydride is used. For other candidates, the decrement of the propellant density jeopardizes the potential gain obtained for I_s [6]. Other data collections are present in the literature which highlight the benefits of using some metal hydrides in chemical rocket applications [7,8]. System-level considerations about such novel ingredients are not so common. Calabro presented a potential replacement of a rocket stage with a chemical-hybrid propulsion unit based on AlH₃ [9]. In this respect, Klotz published a short note based on the Gordon criterion, weighing the effect of propellant density and specific impulse on volume-limited rocket launch systems [10,11]. He concluded that the use of hydrides in first stages is not convenient. Specifically, aluminum hydride performs better than the elemental metal for upper stages while differences are not present for the first stage. It is important to remark that such study did not account for the possible improvements coming from a reduction of agglomeration level and, thus, from higher delivered specific impulse.

Aluminum hydride was described by several authors as a potential ingredient capable of improving rocket performance. May Chan and Johnson presented a

complete study on AlH₃ application with different oxidizers and binders [12]. Alane was provided by SRI International. The authors noted that the samples had high purity, good storage and thermal stability, as well as good compatibility with several chemicals used in propellant compounding. Friction sensitivity was identified as main issue in such compositions. A publication from SPLab research group by De Luca et al. presented several results for use of aluminum hydride in AP-based solid propellants and HTPB-based hybrid rocket fuels [13]. Interesting increments of ballistic properties were evidenced. Metal agglomeration was still present, in a reduced extent. Stability issues were not detected.

The oxidation of aluminum hydride was investigated by Bazyn et al. from both experimental and modeling viewpoints, finding a decomposition-oxidation mechanism [14]. The decomposition into elements is reportedly a one-step endothermic reaction process, as reported in Eq. (1) [15]. The heat of reaction is 11.4 kJ/mol at standard temperature and pressure.



Out of the possible crystalline structures, the α -AlH₃ represents the most stable. Several polymorphs exist which turn into the alpha phase before decomposition, if reacted at 100°C [16].

The preparation of such material was faced by several researchers. Brower et al., in the review section of their paper, listed different methods to prepare alane, spanning from lithium-aluminum hydride reaction with aluminum chloride to the bombardment of ultrapure aluminum with hydrogen ions [17]. Recent attempts to develop a production process of such material are recorded in Europe, USA, China, and Russia, with variable fortune. In the frame of the GRAIL project, CNRS-IC2MP research group is leading the activity on aluminum hydride development while SPLab-POLIMI is characterizing the outcomes. Progresses and status of this topic in the frame of the GRAIL project are presented.

2. PURITY AND PERFORMANCE

Different production techniques can lead to various effects in the final product. Dow Chemical Company produced cubic crystals of aluminum hydride by means of a continuous crystallization methodology. The product is sensitive to the modification of chemical ratios, heating, or timing. The presence of impurities in the solvated phase may jeopardize the process.

The purity of the molecule is an important aspect related to the application of aluminum hydride in propellants since rocket performance is lowered as the amount of hydrogen released by the molecule decreases. Moreover, the stability in time inside the propellant has to be carefully assessed. However, the importance of purity depends upon the type of energetic formulation. Three reference compositions, reported in Table 1, are taken as examples. HTPB inert binder is assumed.

Table 1. Three sub-optimal sample compositions. The fuel is a mixture of aluminum and its hydride. Data are expressed in weight percent

Id.	Oxidizer	Fuel	Binder
A	69 AP	19	12
B	69 ADN	18	13
C	32 ADN/32 AN	23	14

The fuel of such compositions is a blend of aluminum hydride and metallic aluminum. Figure 2 and Figure 3 collect thermochemical results as hydride/metal ratio spans from 0% to 100%. Tested compositions were not specifically optimized for each condition but theoretical drop-in replacement of Al was done. It is known that the addition of hydrides increments the ideal specific impulse. If part of the metal fuel is aluminum, a reduction of the performance is progressively observed. This condition might be representative of a propellant prepared with a partially de-hydrogenated hydride. In the figure, performance of AP-based formulation (label A) is reduced by almost 3% if the overall metal fuel is de-hydrogenated. A composition containing ADN or a blend of ADN and AN is less sensitive on the reduction of hydride concentration and the total performance decrement is

approximately of 1-1.5% for a complete de-hydrogenated condition.

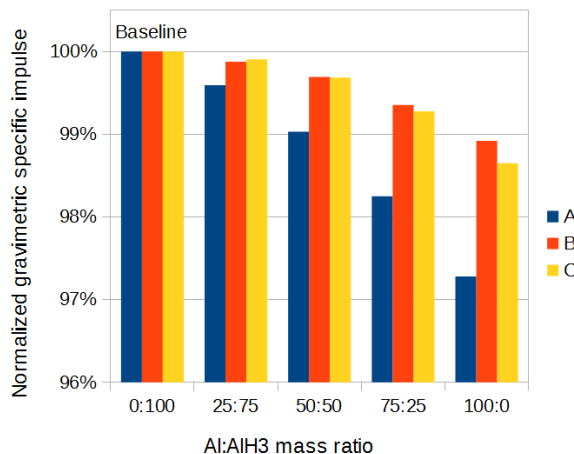


Figure 2. Normalized I_s trend as a function of Al:AlH3 ratio

The limited density of aluminum hydride influences the volumetric specific impulse. In this non-optimal composition the progressive reduction of alane fraction in the fuel causes a progressive increment of the I_v . The reader should be aware that ingredient mass fractions can be optimized for performance improvement.

Within the tested compositions, the propellant based on AN/ADN oxidizer blend suffers from the largest decrement of I_v when aluminum is replaced by alane (label C, about 12% variation). The ADN-based propellant (label B) is the less sensitive among the tested group while AP-based composition (label A) has a variation of about 8%. It is important to underline that computations are assuming the total decomposition of aluminum hydride into aluminum metal and volatile hydrogen, according to Eq. (1). The presence of other impurities is currently neglected.

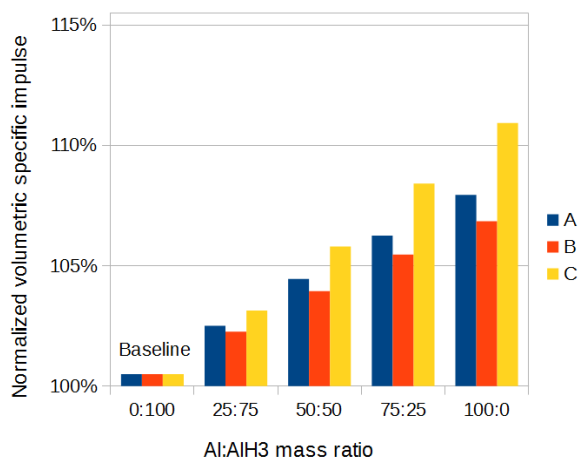
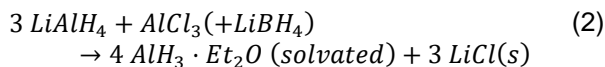


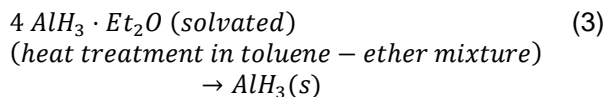
Figure 3. Variation of I_v as alane fraction is modified

3. EXPERIMENTAL

In the frame of the GRAIL (Green Advanced High Energy Propellants for Launchers) project, a research and innovation activity financed in the frame of the H2020 European program, some batches of aluminum hydride have been produced by the IC2MP group, University of Poitiers. The alane samples were prepared by a two-step procedure using an organometallic synthesis method under argon [17,18]. First step reaction is reported in Eq. (2).



After reaction (2) is completed in ether, LiCl precipitate is removed by filtration to yield a clean solution containing aluminum hydride-diethyl ether complex $[\text{Al}(\text{AlH}_4)_3(\text{C}_2\text{H}_5)_2\text{O}]$, excess LiAlH_4 , and LiBH_4 . In order to remove ether in $\text{AlH}_3 \cdot \text{Et}_2\text{O}$ complexes and so to obtain non-solvated alane, the $\text{AlH}_3 \cdot \text{Et}_2\text{O}$ complexes solution was treated:



The solution containing the alane-ether complex and excess LiAlH_4 in the presence of LiBH_4 is added to a balloon containing toluene (see Eq. (3)). Heating the solution leads to evaporate the solvent, mainly ether. Solution temperature is controlled to evaporate most ether so that a white precipitate appears in the solution. Evaporation is undertaken until the collected liquid volume approaches the initial ether volume used in the reaction. Finally, this

solution is cooled to room temperature and filtered. White or grey powder is obtained. This solid is washed with anhydrous ether and dried. An X ray diffractogram (PANalytical “Empyrean”) of the fresh powder thus obtained is depicted in Figure 4 and confirms that pure, crystalline alfa phase was actually obtained.

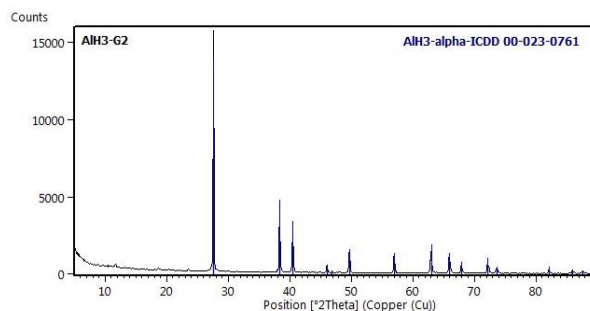


Figure 4 XRD of synthesized alane. Blue vertical lines show reflections of crystalline $\alpha\text{-AlH}_3$

Characterizations performed at the SPLab of Politecnico di Milano focused on material properties. At this stage, available quantities did not allow propellant-level analysis. Thermogravimetric, crystallographic, morphology characterizations have been performed on fresh samples. Some powder was also stored in air under different temperatures (36 °C and 60 °C) and moisture conditions (dry air, 32% Rh, and 75% Rh). Characterizations aimed at monitoring the variation of some peculiar properties after one week and one month. Dry atmosphere was granted by silica gel beads whereas the controlled moisture atmosphere was obtained using a saturated solution of salts.

3.1. Microscopy

Some of the micrographs obtained from SEM imaging are presented in this section. The crystal represented in Figure 5 shows a needled form. A detailed observation of the superficial texture visible in Figure 6 shows the presence of some porous structures. The opening of pores and cracks on crystal surface of hydrides may be caused by dehydrogenation process of the original molecule. Further observations show the presence of other structures having shapes different from the typical cubic arrangement. Both spherical shapes and thin irregular structures are visible in Figure 7. Recognition of such structures was not performed.



Figure 5. SEM analysis of AlH₃ sample

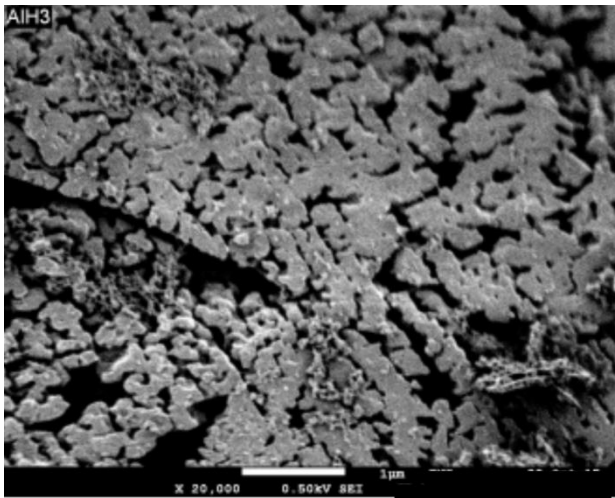


Figure 6. Detail of AlH₃ surface texture

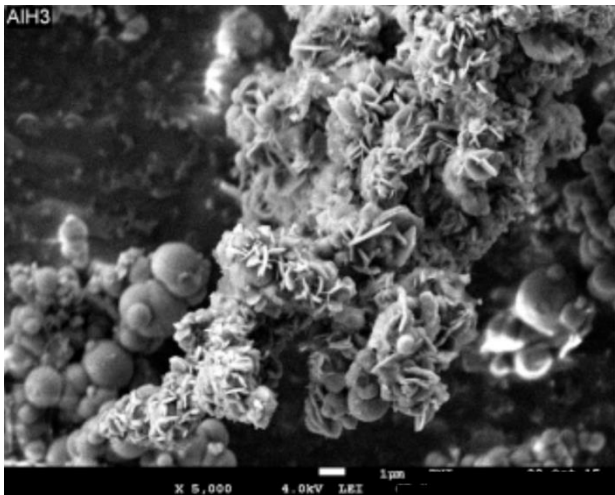


Figure 7. Exotic shapes found in the sample

3.2. Gas release

Aluminum hydride is a hydrogen-storage material. That is, the volume of hydrogen released can represent a valuable experimental data to obtain information on material properties. Samples were reacted with a soda solution in water. We compare the results with the nominal release of hydrogen from a 100% pure aluminum hydride of the same mass. In this last case, computations account for both alane dehydrogenation caused by water contact according to the nominal reaction (1) and aluminum hydrolysis in the soda solution (4), granting a total yield of 3 moles of H₂ per mole of AlH₃ [19].

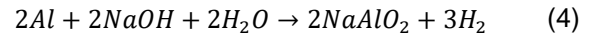


Table 2 reports the results for two tests performed on fresh aluminum hydride samples. For simplicity, molecular hydrogen release is assumed. The table reports the number of moles both measured during the experiment (N_{H_2}) and ideally produced by the same amount of a pure aluminum hydride (N_{H_2-id}).

Table 2. Gas release from alane samples in soda-water solution

Sample mass	N_{H_2}	N_{H_2-id}	$\frac{N_{H_2}}{N_{H_2-id}}$
72.65 mg	1.995e-3	7.265e-3	27.5%
73.77 mg	2.035e-3	7.380e-3	27.6%

3.3. Thermogravimetric tests

Samples were analyzed using a simultaneous DSC/TGA (Netzsch, STA449 F5 Jupiter). Scans were performed in alumina crucibles from ambient temperature to 300°C. The purging gas was argon, having a flow rate of 70 mL/min.

Figure 8 shows the characterization of a fresh sample. The onset at 175°C is about the value reported by Graetz for the decomposition of small crystallites (about 170°C) [16]. The same author reports a higher decomposition onset for material treated with a stabilization process and featured by large particles. The mass loss associated to the main decomposition peak is about 5% but some desorption is still observed in advance, during the whole heating process. From equation (1), we

would expect a decrement of about 10% by mass. Mass decrease is also present after the main decomposition peak. The reason for such mass loss is still under investigation.

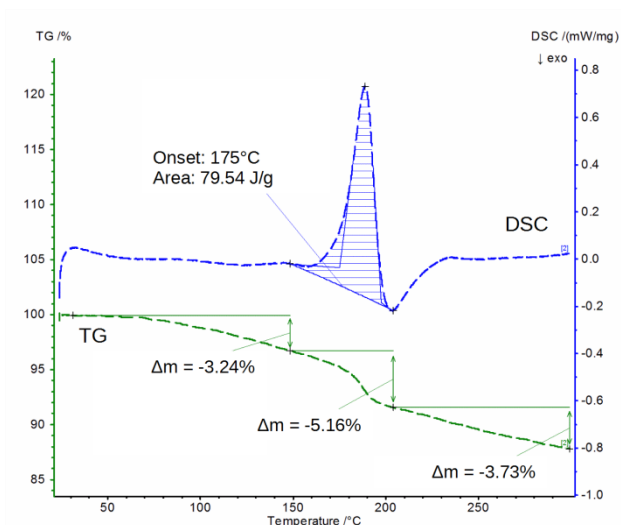


Figure 8. Simultaneous DSC/TGA on aluminum hydride sample

The material is sensitive to moisture exposure, even for short periods. Figure 9 reports the DSC analysis of three samples stored at different moisture levels, at the constant temperature of 36°C. It is possible to see that some exothermic reactions, not present in the fresh sample are generated after storage. The endothermic peak attributed to alane decomposition shifts few degrees ahead (from 175 °C observed in Figure 8 to about 180 °C reported in Figure 9). An endothermic reaction is also present in the second part of the scan. Its buildup follows the moisture level of the storage atmosphere.

The simultaneous trace of TG signals is reported in Figure 10. In the full temperature interval, the mass loss of the sample exposed to the highest moisture level is the highest, probably due to water desorption. However, it is important to associate the largest mass loss to an endothermic peak which is not related to the dissociation of aluminum hydride. The release might be associated to some product derived by water interaction with the material. After 15 days of storage at 36°C the sample preserved in dry conditions showed only minor changes in the DSC trace with respect to the fresh sample. Also in a relatively dry environment (32% Rh) the behavior

of the sample changed, showing that the material is extremely sensitive to the presence of water.

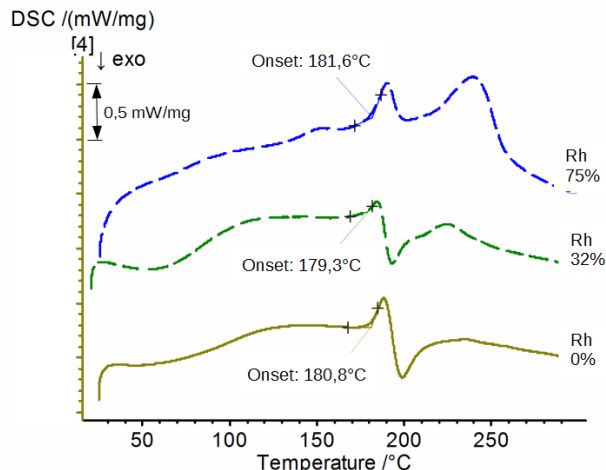


Figure 9. DSC of aluminum hydride after 15 days of exposure to different moisture levels at 36°C. Curves were shifted for better representation.

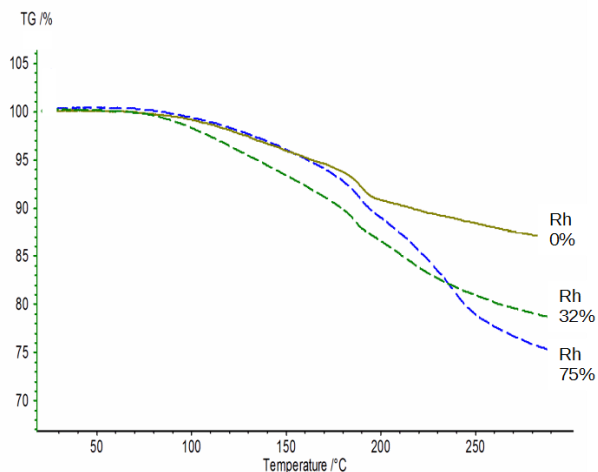


Figure 10. TGA of aluminum hydride after 15 days of exposure to different moisture levels at 36°C

Finally, the effect of storage in dry conditions up to one month at 60°C is reported in Figure 11. It is interesting to note that main changes occurred just after 15 days of the storage process, probably due to the temperature level. Past this initial transient behavior, the sample was stable and did not evolve. The onset of a desorption reaction appears at about 90°C while the peak associated to dehydrogenation becomes weaker and is delayed.

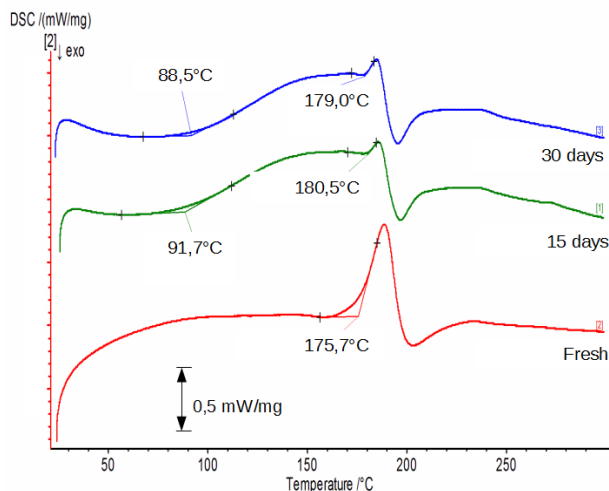


Figure 11. DSC of samples stored under dry conditions at 60°C for different times. Curves were shifted for better representation.

3.4. Structural characterization

The composition of the sample was characterized using XRD technique. Due to the nature of the diagnostic technique, the identification of components is limited to phases which have a crystalline structure. The XRD diffractogram of the material as it arrived to SPLab for analysis is reported in Figure 12. Only aluminum hydride (alpha phase) and aluminum were identified. Quantitative analysis of the crystalline phases identifies 90% of aluminum hydride and 10% of its metal. Average size of coherently scattering domains was 350 nm. This result matched with the data reported in Figure 4, demonstrating that the preparation was not altered by handling and shipment procedures. After moisture exposure, traces of other crystalline compounds arose in the spectrum. In particular, crystalline structures, presumably lithium-containing, became visible. The same analysis was performed also on material stored for 15 days under environmental conditions (without moisture control). Also in this case, spurious peaks appeared only on those samples exposed to moisture. Aluminum hydride remained in the main phase, though a quantitative analysis was not possible. The probable presence of lithium in the sample was not due to a contamination but was confirmed by EDX analysis. The absence in the initial diffractogram may be attributed to the amorphous nature of lithium-based compounds after the production of the alane.

Crystalline phase organizes only after reaction with atmospheric moisture, even at low relative humidity. On this topic, systematic investigations are currently ongoing.

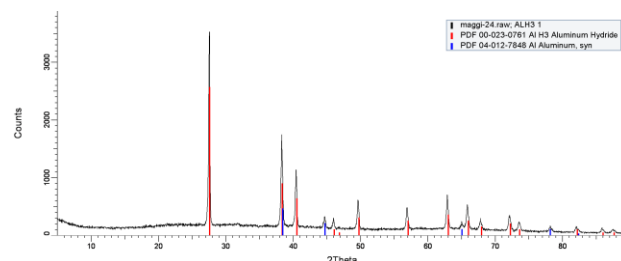


Figure 12. XRD diffractogram of alane sample as received by SPLab.

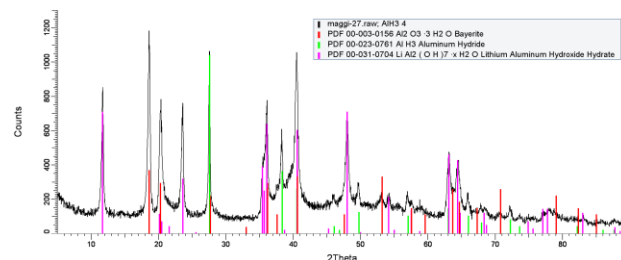


Figure 13. XRD diffractogram of alane sample after 15 days of exposure to ambient conditions

4. CONCLUSIONS

The paper presented a characterization of a batch of aluminum hydride produced by organometallic synthesis. Different morphological, spectroscopic and calorimetric analyses have been performed assessing that alpha aluminum hydride is partially present in the sample. Spurious compounds in amorphous state may be present as well. Calorimetric analyses showed the typical decomposition peak of alane powder, along with other reaction behaviors, still under investigation. Some analyses have been conducted on samples stored under varying moisture and temperature, demonstrating the sensitivity of the original material to the environmental condition and, in particular, to humidity. Further investigations are required to fully understand the behavior of such material under normal storage and inside a propellant batch. Dehydrogenation trends and kinetics should be fully assessed.

5. ACKNOWLEDGEMENTS

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6. NOMENCLATURE

ADN:	ammonium dinitramide
AN:	ammonium nitrate
AP:	ammonium perchlorate
DSC:	differential scanning calorimetry
EDX:	energy dispersive X ray spectroscopy
HTPB:	hydroxyl-terminated polybutadiene
SEM:	scanning electron microscopy
Rh:	Relative humidity
TGA:	thermogravimetric analysis
XRD:	X ray diffraction
I_s :	gravimetric specific impulse, s
I_v :	volumetric specific impulse, kg s/m ³
M_{mol} :	molar mass, g/mol
N_{H_2} :	number of H_2 moles released during hydrolysis experimental characterization
N_{H_2-id} :	number of H_2 moles which a pure sample may release
T_f :	adiabatic flame temperature, K

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