



## Luminescent properties of aluminum hydride

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### ABSTRACT

We studied cathodoluminescence and photoluminescence of  $\alpha$ -AlH<sub>3</sub> – a likely candidate for use as possible hydrogen carrier in hydrogen-fueled vehicles. Luminescence properties of original  $\alpha$ -AlH<sub>3</sub> and  $\alpha$ -AlH<sub>3</sub> irradiated with ultraviolet were compared. The latter procedure leads to activation of thermal decomposition of  $\alpha$ -AlH<sub>3</sub> and thus has a practical implementation. We showed that the original and UV-modified aluminum hydride contain luminescence centers – structural defects of the same type, presumably hydrogen vacancies, characterized by a single set of characteristic bands of radiation. The observed luminescence is the result of radiative intracenter relaxation of the luminescence center (hydrogen vacancy) excited by electrons or photons, and its intensity is defined by the concentration of vacancies, and the area of their possible excitation. UV-activation of the dehydrogenation process of aluminum hydride leads to changes in the spatial distribution of the luminescence centers. For short times of exposure their concentration increases mainly in the surface regions of the crystals. At high exposures, this process extends to the bulk of the aluminum hydride and ends with a decrease in concentration of luminescence centers in the surface region.

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### 1. Introduction

Aluminum hydride ( $\alpha$ -AlH<sub>3</sub>), due to high hydrogen content by volume (148 g/L) and mass (10 wt%) is a likely candidate for use as possible hydrogen carrier in hydrogen-fueled vehicles [1]. The main process leading to the formation of free hydrogen is thermal decomposition of aluminum hydride. It was previously shown [2] that at temperatures of 70–120 °C the active hydrogen evolution from aluminum hydride is preceded by a long incubation phase. Its duration (from tens of minutes to days) depends on the temperature of samples. The main problems that hamper practical use of aluminum hydride are associated with the need to reduce the temperature of the dehydrogenation and duration of the incubation period. Numerous attempts based mainly on mechano-chemical activation were made to reduce the temperature of the dehydrogenation [3,4]. We hypothesized and showed that improvement of the kinetic characteristics can be achieved by preliminary exposure of aluminum hydride to a ultraviolet (UV) radiation [5,6]. It was shown that UV activation leads to a reduction in incubation time due to generation and clustering of hydrogen vacancies.

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Use of luminescence methods helped greatly in interpretation of the results of UV activation of aluminum hydride decomposition, understanding of processes occurring during incubation, and development of the activation model [6]. The aim of this work was to obtain additional information about electronic structure of aluminum hydride and its transformation in the course of optical activation using methods of cathodoluminescence (CL) and photoluminescence (PL). We assume that it will be useful in the development of practical activation procedure. In addition, we believe that the published results are of general interest to condensed matter physics, as they are obtained by application of the CL and PL methods to metal hydride, the material rarely used in such studies. Luminescent properties of UV activated aluminum hydride may be of interest in the context of the theory of phase transformations concerning the study of the mechanisms of formation of new phase nuclei in the volume of the parent phase.

In addition to luminescence methods in this paper we used the density functional theory (DFT) method to calculate the absorption spectrum of the ideal  $\alpha$ -AlH<sub>3</sub> crystal. Comparison of the calculated data with the luminescence results allowed arguing that in the energy range of 1.5–4.5 eV defects in the structure of aluminum hydride act as the source of luminescence.

## 2. Samples and experimental technique

In the present study, we investigated the  $\alpha$ -phase of  $\text{AlH}_3$  crystal, which is the most stable polymorph of  $\text{AlH}_3$  under normal conditions [7,8] and crystallizes into a lattice with the trigonal space group  $R\bar{3}c$  ( $D_6^{3d}$ ). Hexagonal unit cell (UC) of  $\alpha$ - $\text{AlH}_3$  with lattice parameters  $a=4.449 \text{ \AA}$  and  $c=11.804 \text{ \AA}$  [7] contains six formula units. Band structure calculations [9] showed that the  $\alpha$ - $\text{AlH}_3$  crystal has a direct band gap 3.54 eV, which is located at  $\Gamma$ -point of the Brillouin zone.

Samples of  $\text{AlH}_3$  used in our study were made by means of wet chemistry. Description of synthesis procedure can be found in [10]. They have form of a powder consisting of cubic particles with an edge length of 10–15  $\mu\text{m}$ . SEM images can be found in [1,2]. Samples were stored in argon atmosphere, but prior to the study they were exposed to air for a long time. Special experiments showed that duration of air exposure does not influence desorption kinetics. Similar results are reported in [11]. UV irradiation (details on which may be found in the end of this section) changes the desorption properties of aluminum hydride. However, spectra obtained for two samples subjected to the same 2-h irradiation procedure after 20 min and 20 h after end of irradiation are identical. Similar experiments but for vacuum irradiation were described earlier in [12]. They show agreement between desorption curves obtained after 10, 30, 60 min and 96 h after the end of the same 30-min UV irradiation procedure. Also luminescence spectra in this study did not show dependence on the duration of exposure of aluminum hydride to air. All this provides a good evidence of stability of desorption and luminescence properties of material under study.

Scanning electron microscope Zeiss SUPRA 40VP with cathodoluminescence registration system Gatan MonoCL3+ was used in the CL experiments. Spectral registration was carried out in the range of 250–800 nm by continuous scanning with the electron beam of the sample surface. Each spectrum was recorded at a different location in the sample. Width of the scanning area was 30  $\mu\text{m}$ . Duration of each registration was 1 s. Spectral resolution was 2 nm. Energy of the electrons that excite the luminescence was 5–30 keV. Beam current varied from 0.4 to 11 nA.

The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were registered by the Fluorolog<sup>®</sup>-3 unit, manufactured by HORIBA Jobin Yvon. The excitation was carried out by 450 W xenon lamp. In the PL experiments a series of PL spectra with excitation at wavelengths of 275 nm (4.51 eV); 300 nm (4.13 eV); 325 nm (3.81 eV); 350 nm (3.54 eV); 375 nm (3.31 eV); 400 nm (3.1 eV) were obtained. The width of the gap in excitation monochromator was 10 nm, and 3 nm in registration monochromator. PL spectra were recorded in the range determined by the excitation wavelengths as  $(\lambda_{\text{ex}} + 30 \text{ nm})$  to  $(2\lambda_{\text{ex}} - 30 \text{ nm})$ , to eliminate the influence of second order effects. Luminescence excitation spectra were recorded at 350 nm (3.54 eV); 440 nm (2.82 eV) and 550 nm (2.25 eV). In this case, the width of the gap in the excitation monochromator was 3 nm, and 1 nm in the registration monochromator. We investigated the original  $\alpha$ - $\text{AlH}_3$  and  $\alpha$ - $\text{AlH}_3$  preliminary irradiated with UV for 15, 30 and 60 min. The spectra were adjusted for the spectral sensitivity of the equipment and the intensity of the excitation lamp. All measurements were carried out at room temperature.

UV irradiation of aluminum hydride powder for the purpose of decomposition activation (photomodification) was carried out by a mercury lamp in air at room temperature. Samples for CL were irradiated on the vibrating table for a long period of time, which ensured photomodification of each particle. Samples for PL were irradiated without additional stirring. As a result, the upper particles were shadowing lower ones. In the latter case both the

quantities of  $\text{AlH}_3$  powder and exposure times were smaller than in the former. In [6] it was shown that only one line of a mercury lamp spectrum with an energy of 4.88 eV (254 nm) has an activation effect in the course of UV irradiation in air atmosphere.

## 3. Results and discussion

### 3.1. Luminescence of as-received $\alpha$ - $\text{AlH}_3$

Fig. 1 shows typical CL spectral curves of aluminum hydride. CL of aluminum hydride was observed in the energy range of 1.5–4.5 eV. The shape of the spectrum is almost independent of the excitation energy and the density of the excitation current. Luminescence intensity in the first approximation is proportional to the excitation current in the entire spectral range and increases along with the energy of the exciting electrons.

Implementing the mode where excitation energy is invariable ( $E_0 \cdot I_0 = \text{constant}$ ,  $E_0$  – beam energy,  $I_0$  – beam current) [13] shows that the highest CL emissivity is registered when luminescence centers (LC) in the near-surface region of the samples are excited (see Fig. 1). At the same time, the relatively high intensity at energies of exciting electrons of 30 keV indicates the existence of LC in the bulk of the test samples as well. Comparison of the form

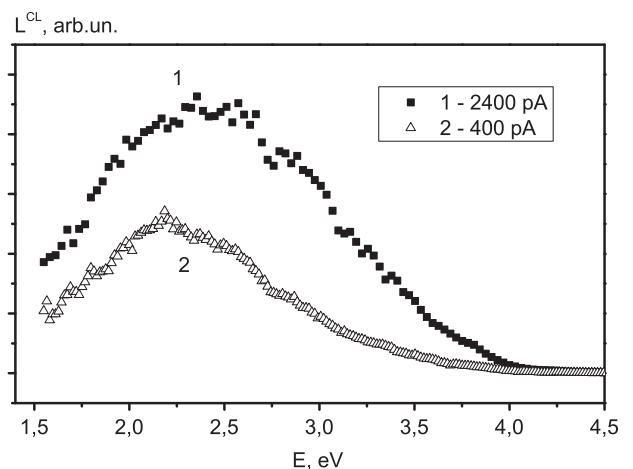


Fig. 1. CL spectra of  $\alpha$ - $\text{AlH}_3$ , obtained in the mode where excitation energy is invariable with energies of 5 keV (1) and 30 keV (2). Flow density values are provided in the legend.

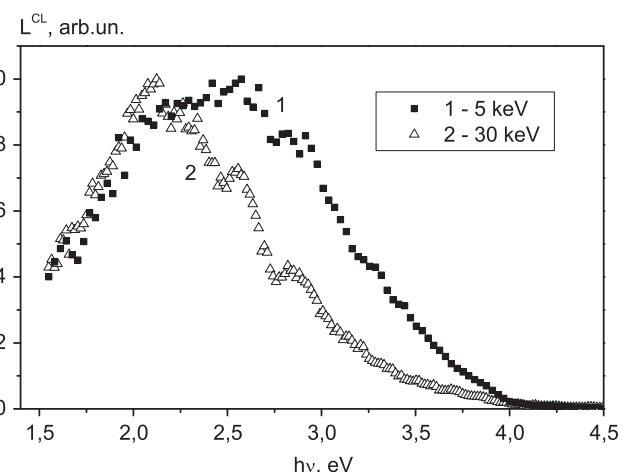


Fig. 2. Normalized CL spectra of  $\alpha$ - $\text{AlH}_3$  with excitation energies of 5 keV (1) and 30 keV (2).

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