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**SECTION: PHYSICS**

# An investigation of AlN nanoparticles by DTA and DTG methods

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**Abstract**

Differential thermal analysis (DTA) and differential thermal gravimetry (DTG) studies at different heating rates of were considered for AlN nanoparticles. The free Gibbs energy in the temperature range of 300÷1400 K is determined at 5, 10, 15 and 20 K/min heating rates. Experiments were separately carried out in both heating and cooling processes and obtained results were analyzed in detail. The enthalpy and entropy of the system composed of nano AlN particles at different thermal treatment rates were calculated (theoretical calculations were justified by experimental results). The values acquired from the experimental results were compared for all thermophysical parameters at different thermal treatment rates.

***Keywords:*** AlN nanoparticles, thermal parameters, thermal gravimetry, Gibbs energy, enthalpy.
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## 1. Introduction

AlN is one of the promising material that has a very interesting physical properties. Although the wide band gap (~ 6 eV), AlN demonstrate excellent optical properties like semiconductor material [1-7]. Moreover, high chemical stability, high melting point and excellent crystallinity degree allow using it in the various filed of science and technology. Due to the excellent properties of AlN is widely studied by researcher [8-16]. In particular, high stability at higher temperatures is provide important applications in nuclear, as well as aviation and space technologies.

It is known that the study of physical properties is key method to investigate application perspectives of the materials. In this regards, an investigation of thermal parameters are important way to study of the materials. As mentioned above, due to the high stability of the AlN, it is very interesting to investigate the thermophysical parameters. Although the thermal parameters of nano AlN were investigated in our previous works [16, 17], some details are also considered in this study. The result of the diferential thermal analysis and diferential thermal gravimetry are discussed in detail. Based on the experimental results, the enthalpy and entropy in the nano AlN were calculated weat different thermal treatment rates were calculated (theoretical calculations were justified by experimental results). The values acquired from the experimental results were compared for all thermophysical parameters at different thermal treatment rates.

## 2. Experiments

Nano AlN particles with particle size 65-75 nm, and 99+% purity were taken as the research object. The experiments were performed on the "DSC/TGA3+" device produced by Metler Toledo. Operating range of this device is 290 K-1400 K, thermal treatment rates were selected as 5, 10, 15 and 20 K/min. In order to remove combustion products from the system and to prevent the condensation process, argon inert gas was used and supplied to the system with 20 ml/min rate. A standard aluminum-oxide-based pan was used. The mass of the sample is determined with an electronic recording device placed on the thermocouple with $\pm 10^{-6}$ g accuracy. The difference between the sample-filled pan and empty pan weights were automatically recorded. All results obtained in the experiments and later according to the theoretically calculated values are graphically depicted in the "Origin Pro 9.0" program.

## 3. Results and discussion

In the presented work, nano AlN particles were studied separately in heating and cooling processes in the temperature range of 300 K – 1400 K with four different heating rates (5 K/min, 10 K/min, 15 K/min and 20 K/min). DTA and DTG spectra of AlN nanoparticles at all thermal treatment rates (5 K/min, 10 K/min, 15 K/min and 20 K/min), Gibbs energy, enthalpy and entropy of the system were theoretically calculated based on experimental results. Figure 1 briefly shows the DTA and DTG spectra corresponding to the thermal treatment rates of 5 K/min and 20 K/min during the heating processes.

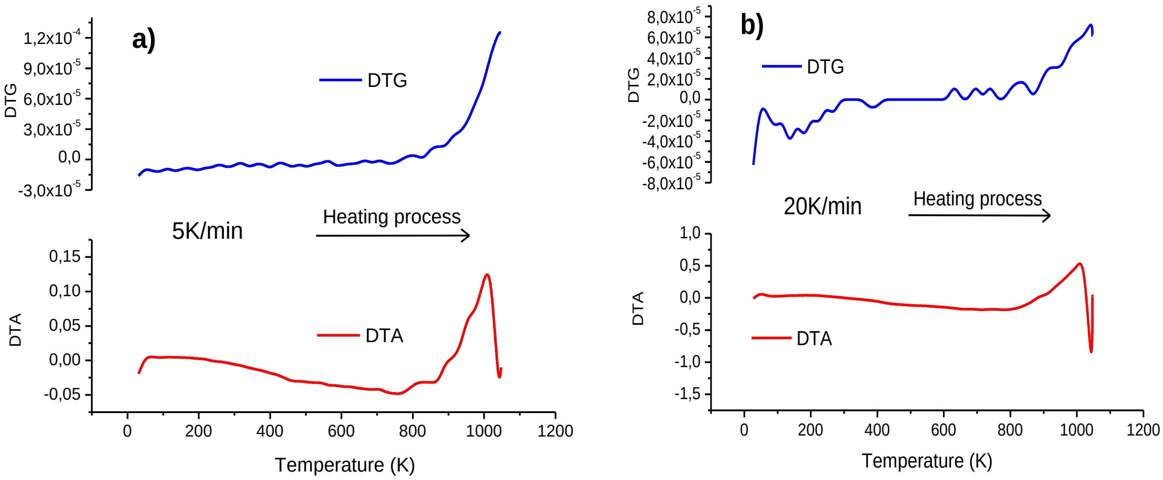


**Figure 1.** DTA and DTG spectra of heating process at different rates of thermal treatment of AlN nanoparticles (a – 5 K/min, b – 20 K/min).

In the first approach consider the heating process (Figure 1 a, b). During the heating process, as can be seen from the spectra, it is observed that water adsorbed from the atmosphere or other additional elements leave the system. As can be seen from the heat flux spectra, at a temperature of about 750 $^0$C the first stage of this process ends. It's known that nanomaterials have a very large specific surface area (SSA) and these types of materials are surface active, which makes water or other compounds suspended on the nanoparticle surface immediately upon contact with the atmosphere. The active surface is chemisorbed by $H_2O$ and OH groups from the environment in a weak interaction. A linear increase in temperature breaks down the weak repulsive effect. From the observation of the thermal curves, it can be concluded that as a result of the temperature increase, the suspended water or other impurities present in the nanomaterial begin to leave the system.

As can be seen from the DTG curves, the complete completion of this process corresponds to the temperature values of approximately 750 $^0$C (Figure 1 a, b). As can be seen from the DTG spectrum, in the part of the temperature after 750 $^0$C, an increase in the mass is observed, which can be explained by the oxidation of the nanomaterial. It is important to note that the oxidation process here is the combination of oxygen adsorbed from the environment with AlN nanoparticles, which increases the mass.

During the cooling process, an increase in the minimum value of the temperature in the mass is observed, which is probably related to the sorption process (Figure 2 a, b). In both processes, heat flux from DTA spectra confirms the direction of the process. Thus, the peaks observed in the DTA spectra characterize the energy used in the process or the energy released from the process. Confirming the peak mass increase observed in the DTA spectra at the end of the cooling process, it shows that the nanoparticles are re-adsorbed from the atmosphere (Figure 2b).

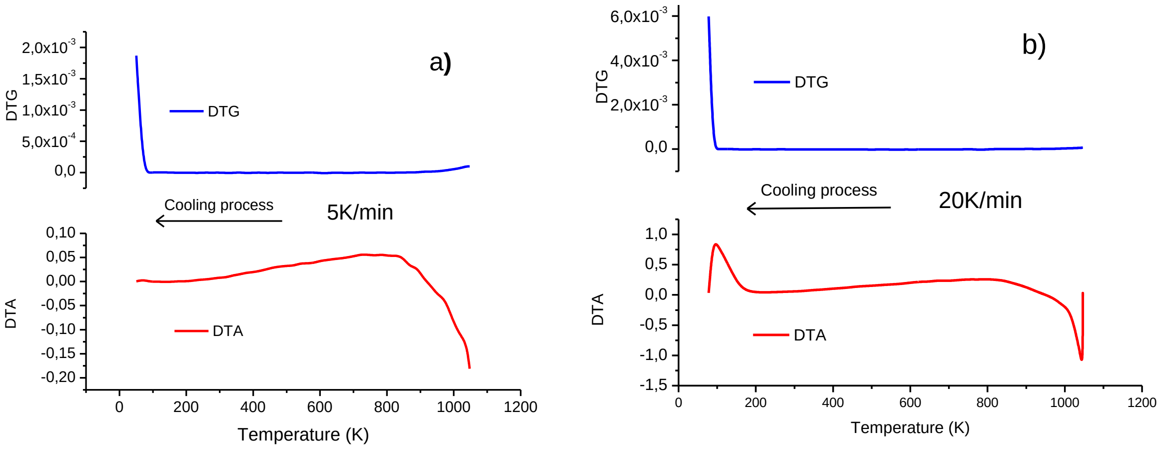


**Figure 2.** DTA and DTG spectra of cooling process at different rates of thermal treatment of AlN nanoparticles (a – 5 K/min, b – 20 K/min).

Temperature dependences of entropy and enthalpy of AlN nanoparticles at different thermal processing rate (with $\Delta\beta$=5 K/min steps) are also studied, and obtained results confirmed our previous work [16]. The entropy of the system increases with the increase of thermal treatment rates.

The enthalpy and entropy of the system become negative after the temperature of approximately T≥600 K. This situation can be explained by exothermic effects in approach. Peaks observed in entropy and enthalpy in both heating and cooling processes can be explained as oxidation and reaction products leaving the system. The amount of chemical products leaving the system and the amount of the oxidized sample equalize at a temperature of 1200 K. And at temperatures greater than 1200 K, the amount of reaction products leaving the system exceeds the amount of the sample entering the reaction. As a result of this, peaks are observed at 1200 K in the temperature dependence of entropy and enthalpy in both heating and cooling processes. The temperature dependences of the free Gibbs energy calculated according to the experimental results in the heating and cooling processes are depicted in Figure 3. As can be seen from the figures, the numerical value of the free Gibbs energy depends inversely on the rate of thermal treatment in both processes (Figure 3a).

With the increase in the rate of thermal processing, the numerical value of the free Gibbs energy decreases, which is an indicator of the less stable system during heating with relatively low rates. As can be seen from the dependences obtained in wide temperature ranges, the numerical value of the free Gibbs energy increases almost directly proportional to the temperature up to the value of 1200 K. An increase in the numerical value of the Gibbs free energy for a system isan increase in the system's potential energy (chemical potential). Any system reduces to minimize its potential energy over time and an increase in the value of

Gibbs free energy in any system can lead to a decrease in the stability of that system. Physically, this explains that the stability of the system naturally decreases at higher temperatures.

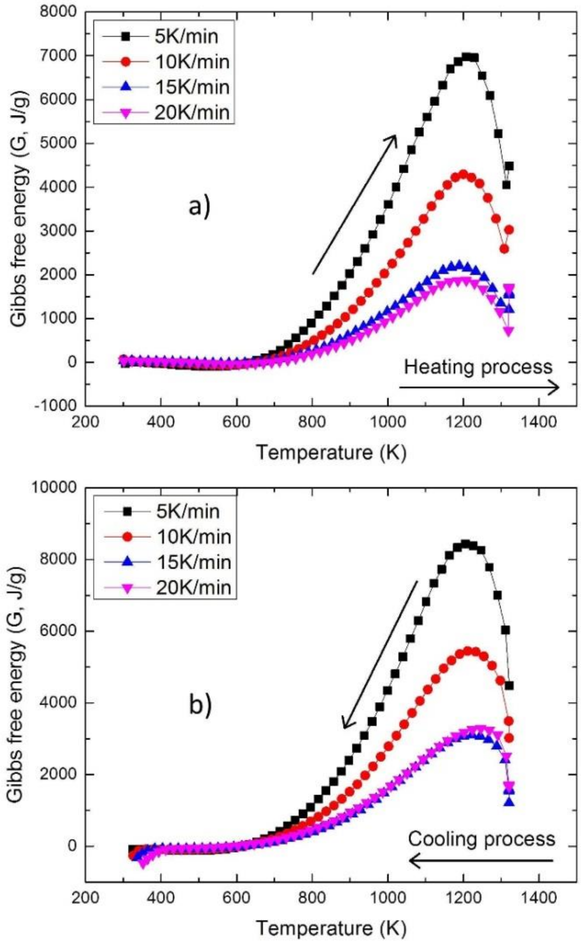


**Figure 3.** Temperature dependences of free Gibbs energy in the heating and cooling processes of nano AlN particles at different thermal treatment rates (a heating process, b cooling process).

According to the experimental results, the numerical value of the free Gibbs energy takes zero or negative values in the region of low temperatures such as T<600 K.This means that the processes occurring in the system are spontaneous and the system can move towards equilibrium. On the other hand, at temperatures T<600 K, in the general approach, the numerical value of the free Gibbs energy changes around zero, which is an indication that the system is in equilibrium. At temperatures T>600 K, the numerical value of free Gibbs energy is positive. In this case, the processes occurring in the system are not spontaneous, but changes in the opposite direction towards a spontaneous system can be observed.

## 4. Conclusion

Based on the results of the entropy and enthalpy analyses, it was found that the oxidation process is started in AlN nanoparticles after 750 K. However, DTG curves proved that additional trace elements leave the system, which causes the mass to decrease when the temperature increases up to 1200 K. From the temperature T>1200 K, the oxidation process became stronger than the impurities leaving the substance and the mass begins to increase. In both heating and cooling processes, the equilibrium state at 1200 K temperature was determined from Gibbs energy, entropy and enthalpy curves. According to the calculated Gibbs free energy, it is known that AlN nanoparticles are spontaneous or more stable at relatively low temperatures. It was determined that the numerical value of the free Gibbs energy decreases with the increase in the rate of thermal treatment. The decrease in the numerical value of the Gibbs free energy directly explains the stability of the system.

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