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Effect of Homolog Doping on Surface Morphology and Mass-Loss Rates from PETN Crystals: Studies using Atomic Force Microscope and Thermogravimetric Analysis

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Abstract: Pentaerythritol tetranitrate (PETN) is an important energetic material, whose performance as a secondary explosive depends strongly on the density as well as flow porosity of powdered material, which in turn is governed by the size and surface properties of the PETN crystallite particles. Historically there has been evidence that the surface properties of PETN particles can be strongly influenced by the presence of homolog impurities of PETN, in particular, dipentaerythritol hexanitrate (diPEHN) and tripentaerythritol octanitrate (triPEON), although not many systematic studies characterizing such influence exist. In this work we employ thermogravimetric analysis (TGA) to measure mass-loss rates at elevated temperatures and show that doping with a small amount of diPEHN and triPEON can reduce the mass-loss rate from PETN single-crystal surfaces by as much as 35% as compared to undoped crystals. Arrhenius plots of mass-loss rates as a function of temperature suggest that the reduction in evaporation is not due to the change in activation barrier of the molecular evaporation process, but perhaps due to the impedance to the receding motion of the steps by the immobile impurities on the surface. Removal of surface impurities through gentle washing with ethanol leads to enhanced mass-loss rate relative to pure PETN suggesting a roughened surface morphology. Some surface roughening in doped crystals is supported by Atomic force microscopy (AFM) images of growth layers that show evidences of growth layer stacking and rough edges. We also find that a larger amount of impurity added to the original solution does not necessarily lead to a more highly doped crystal, which could perhaps be interpreted as PETN crystals being able to accommodate only up to a certain weight percent of homolog impurities.

Keywords: Single crystal · PETN · Doping · Impurities · Mass-Loss rate · Morphology

1 Introduction

Organic molecular crystals are a topic of great interest in academia, government laboratories, and various industries for a multitude of applications ranging from pharmaceutical and electrical industries to energetic materials. While the presence of a small amount of unwanted impurities in the crystal growth process is not unusual, in many cases impurities are added intentionally with the aim of attaining a material with tailor-made properties. The presence of a small amount (ppm level) of impurities in the growth medium can affect crystal growth kinetics due to the incorporation of impurities on the growth surface. This can significantly impact crystal properties, as has been investigated in detail for various types of organic and inorganic crystals [1–7]. Atomic force microscopy (AFM) imaging has revealed morphological changes in the growth center in the presence of impurities [8–10]. Impurities have also been shown to alter the thermodynamic properties of singles crystals [11].

Interaction between the crystal matrix and impurities depends on the chemical nature of the crystal compound as well as the impurity in question. Impurities can be classified into one of several categories, e.g., anions, metallic cations, polyelectrolytes, surfactants, tailor-made additives, and so on [12]. In addition, the impurity distribution map within the doped crystal could depend on the impurity concentration. Thus, at low concentrations impurities might be adsorbed primarily at the kink sites or at the step edges of crystallite surfaces, while at high concentrations they could be randomly distributed in the bulk matrix [13, 14].

Pentaerythritol tetranitrate (PETN) is a nitrate ester, a very powerful energetic material, and is used as a secondary explosive in military applications and in mining. The performance and properties of PETN can change upon long-term aging due to coarsening that is marked by a gradual decrease in its specific surface area [15, 16]. Previ-

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ous works have demonstrated that doping with appropriate compounds can control such aging process of PETN [11,17,18]. For instance, it was shown that doping with homologs like dipentaerythritol hexanitrate (diPEHN) and tripentaerythritol octanitrate (triPEON) can lower the vapor pressure of PETN single crystals [19]. However, the associated effects on the crystal morphology and mass-loss properties were not addressed.

In this paper we re-analyzed the mass-loss (i.e. sublimation) rates from a series of single crystals of PETN, both pure and the ones grown from solutions, in which a controlled amount of diPEHN and triPEON were added. In order to shed light on the distribution of impurities on the crystal surface and their effect on the surface morphology/roughness we also measured mass-loss rates after washing the crystals with ethanol, with the idea that a comparison between pre-washed and post-washed crystal should provide relevant insights. Finally, we imaged several doped and undoped crystal surfaces with AFM in order to characterize differences in surface features brought about the homolog additives.

2 Experimental

Pure and doped PETN crystals were grown by solvent evaporation. To do this, PETN powder was dissolved in acetone in scintillating vials. The solvent was allowed to evaporate away slowly forming a supersaturated solution, from which crystals grew in the bottom of the vial. PETN, diPEHN, and triPEON were provided by Lawrence Livermore National Laboratory. Pure and doped crystals were used for collecting the rate of sublimation data in a thermogravimetric analyzer (TGA) from 105 °C to 125 °C in steps of 5 °C in the presence of nitrogen as the purge gas (flow rate 15 $cm^3 min^{-1}$). Mass loss at each temperature was measured as a function of time in the TGA (Model – i1000 supplied by Instrument Specialist Inc). Optical images of the crystals were collected before running the samples in the TGA in order to measure the surface area of the crystals. "Image J" software was used to analyze the optical images. The rate of sublimation was normalized by the surface area of the crystal. Morphology of the crystal surface was studied using a Nanoscope IIIa multimode scanning probe microscope (Veeco Instrument Inc., Santa Barbara, CA) operating in contact mode. WSxM software was used to process the images from the scanning probe microscope.

3 Results and Discussion

Figure 1 plots the ratio of the sublimation (i.e., mass-loss) rates of doped and pure crystal within the temperature range of 105–125 °C. For diPEHN doping [Figure 1(top)], it appears that 1000 ppm doping leads to an approx. 20% decrease in the mass-loss rate as compared to pure PETN,

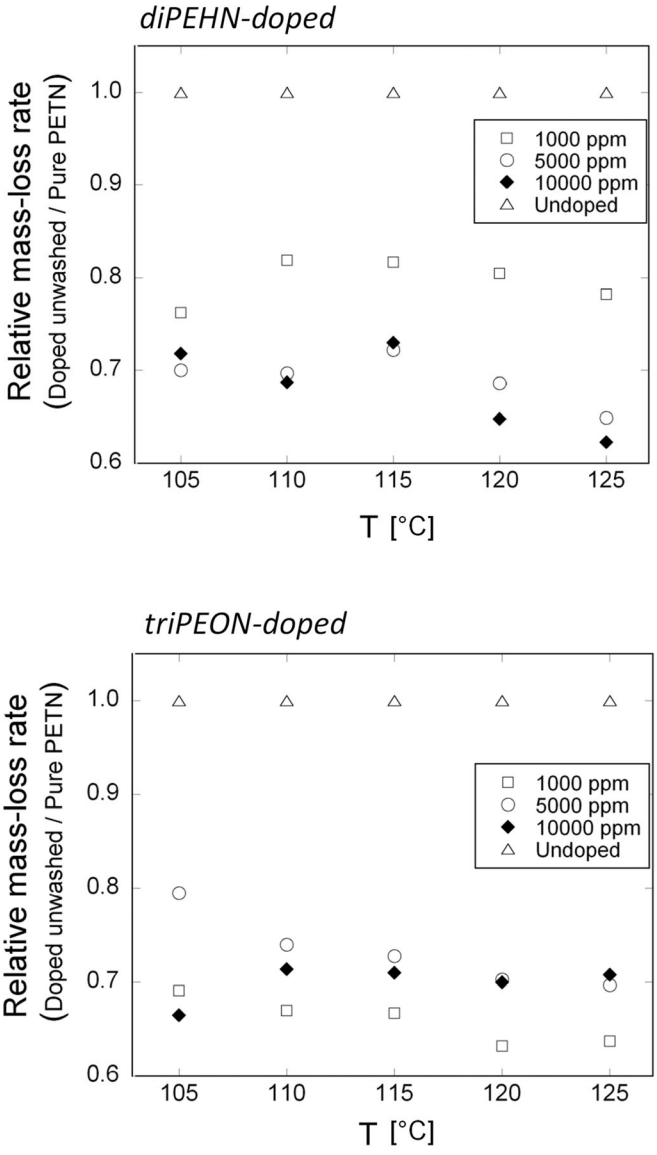

Figure 1. Mass-loss rates of doped PETN *relative* to undoped PETN at various temperatures between 105–125 °C: (top) diPEHN-doped, and (bottom) triPEON-doped. The sample-to-sample variation of the relative mass-loss rates in all cases is approx. 0.1.

while both 5000 ppm and 10000 ppm lead to an approx. 30–35% decrease. As for triPEON doping [Figure 1(bottom)] the reduction of mass-loss rate appears to be higher at the 1000 ppm doping level as compared to 5000 ppm or 10000 ppm doping levels. Thus at $\delta = 1000$ ppm triPEON doping there is approx. 30–35% reduction in mass-loss rate, while at 5000 and 10000 ppm doping levels, the reduction is approx. 30% or slightly lower. These results suggest that the doped crystal can only accommodate a maximum amount of homolog impurities, i.e., approximately 5000 ppm of diPEHN and between 1000 ppm and 5000 ppm of triPEON. Such a picture is also consistent with a limited number of studies, in which we added

10000 ppm of diPEHN + 10000 ppm of triPEON. Crystals grown from such solution exhibited mass-loss rates of only 20–30% lower as compared to pure PETN.

Before proceeding further, we would like to point out that there is a large sample-to-sample variation in the measured mass-loss rates, of the order of approx. 0.1 (i.e. 10%) in the relative rates. Thus, given only a limited number of measurements, a formal statistical analysis of the data using both a parametric test (ANOVA) and a non-parametric test (Kruskal-Wallis) yields no *statistically significant* difference between the various doping levels (at any given temperature) either for diPEHN or for triPEON doping. Nevertheless in the discussion below we try to make good use of the available data and attempt to draw semi-quantitative conclusions for the small-sample-averaged mass-loss rates as a function of impurity-level and temperature.

Figure 1 also shows that the reduction of mass-loss rate does not have any systematic dependence on temperature, irrespective of the homolog or the doping level. This raises the following possibilities: (1) the mass-loss reduction values at these elevated temperatures could also be extrapolated to room temperatures; and (2) the mechanism of mass-loss reduction is likely not through an increase in the effective heat of molecular desorption (sublimation), because if it were, the level of reduction would be strongly decreasing with increasing temperature.

In order to directly test point (2) above, Figure 2 plots the observed mass-loss rates (*y* axis log-scale) from doped PETN crystals (as well as pure PETN) as a function of 1/*T*. The negative slope of such a plot is equal to the molecular heat of sublimation. From the plots in Figure 2 it appears that the heat of sublimation remains essentially unaffected by either the dopant (i.e., diPEHN or triPEON) or the doping level, i.e., 1000, 5000, or 10000 ppm, and the sublimation heat remains approx. 146 kJ mol^{-1}, a well-accepted value for pure PETN. Thus, it would appear that the homolog-induced changes in mass-loss rates happen through the impedance to step motion due to the presence of surface impurities. To gain further insight, we gently washed the doped crystals with ethanol and compared the mass-loss rates from the washed crystals with those of the unwashed crystals. Figure 3 displays: (a) the ratio of mass-loss rates from the washed crystals to that of pure PETN (left top and left bottom); and (b) the ratio of mass-loss rates between unwashed and the washed crystals (right top and right bottom). Some results of note from Figure 3 are:

(1) As compared to pure PETN the washed crystals have distinctly *higher* mass-loss rates. For diPEHN-doping levels of 5000 ppm the increase in washed crystals is as much as approx. 80%, while 10000 ppm doping produces 40–60% increase. Doping with 1000 and 5000 ppm triPEON followed by washing produces 40–60% increase in mass-loss rate relative to pure PETN, while 10000 ppm produces much less increase;

(2) As compared to washed crystals, the unwashed crystals have much lower mass-loss rates, as low as 30–40% for 5000 ppm diPEHN and 40–50% for 1000 and 5000 ppm triPEON;

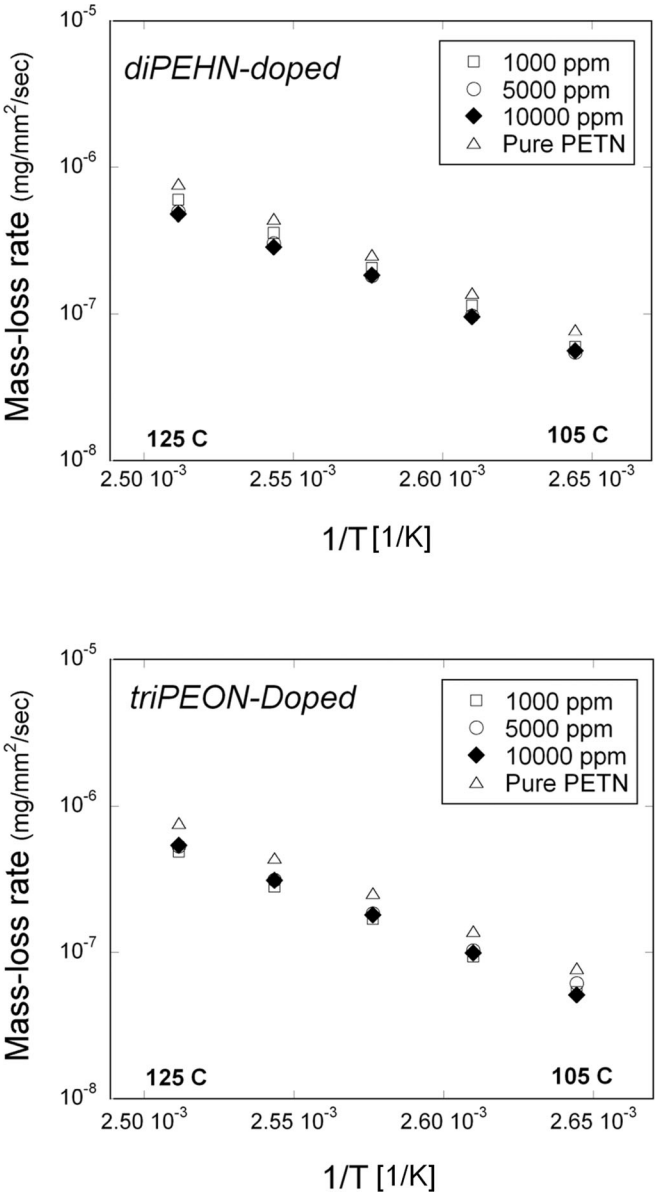

Figure 2. Absolute mass-loss rates (in mg mm^{-2} per s) of (top) diPEHN-doped, and (bottom) triPEON-doped PETN as a function of T^{-1}, showing overall Arrhenius behavior in all cases. The slope in all cases is around 146 kJ mol^{-1}, the known heat of sublimation for pure PETN.

(3) The mass-loss ratio in unwashed vs. washed crystals is close to 1 for undoped (i.e. pure) PETN crystals. This supports the notion that gentle washing with ethanol produces topological surface features in the washed crystals similar to those existing in the pre-washed crystals.

The above results lead to the picture that up to a certain doping level (approx. 5000 ppm for diPEHN and even lower for triPEON) a sizeable amount of these homolog impurities get incorporated on the crystal surface. The presence of

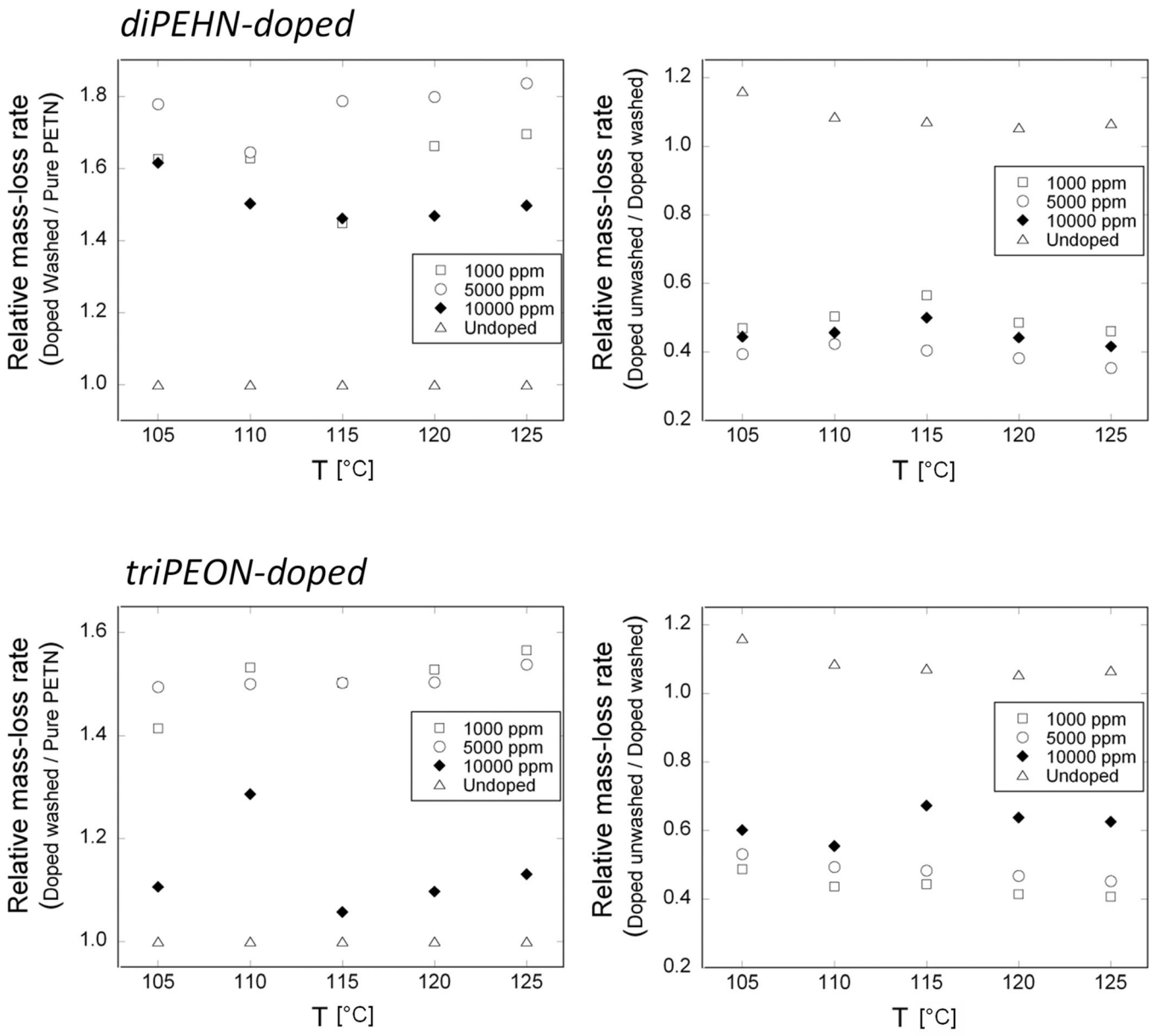

Figure 3. Effects of washing on mass-loss rates: (top left) mass-loss rates of washed, diPEHN-doped crystals relative to unwashed, undoped PETN crystals; (top right) mass-loss rates of washed, diPEHN-doped crystals relative to unwashed crystals of the same doping; (bottom left and right) similar graphs for triPEON-doping.

these relatively immobile impurities impede the motion of PETN steps, potentially leading to a roughened surface topology characterized by irregular step geometries, bunched steps, and so on. Prior to washing, the impurities at the surface lower the mass loss by impeding the motion of the steps, while after washing the rougher surface without any impeding impurities lead to a higher mass-loss rate. At the same time, higher doping levels (e.g., 10000 ppm diPEHN or triPEON) do not necessarily imply higher surface concentration of impurities – the excess impurities could either get incorporated within the PETN bulk or possibly segregate as homolog-rich domains outside the crystal. At this time we can only speculate on this point, and more experiments need to be done to be more definitive.

To look for direct evidence of roughening in doped crystals we took AFM images of the surfaces of both pure and doped PETN crystals. An ex situ AFM investigation was conducted on the flat surface of pure and doped PETN crystal. Figure 4(a), (c), and (e) presented AFM images of the $<110>$ face of the pure PETN, 1000 ppm diPEHN doped, 5000 ppm triPEON doped crystals, respectively. Figure 4(b), (d), and (e) showed the height profile of the growth layers of pure, diPEHN and triPEON doped PETN, respectively. Height profile showed that doping of diPEHN and triPEON

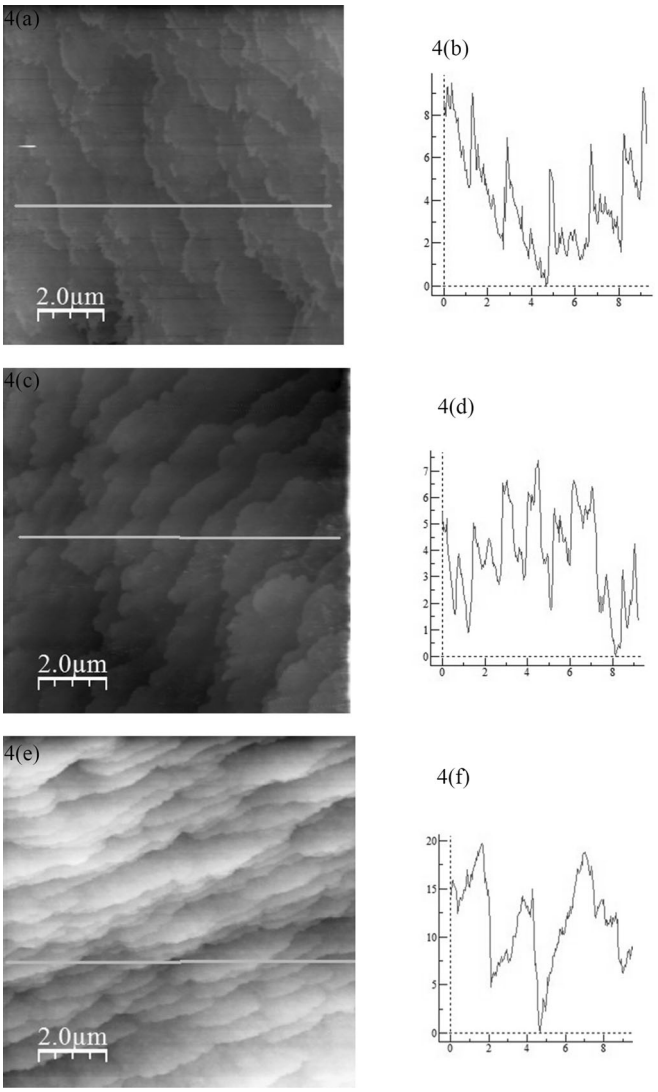

Figure 4. AFM images of the <110> faces of: (a) pure PETN; (c) diPEHN-doped PETN; (e) triPEON-doped PETN crystal. Height profile of the growth layers of (b) pure PETN; (d) diPEHN-doped PETN; (f) triPEON-doped PETN crystal.

increased the step height of growth layer. Average steps height for PETN was found to be around 3 nm, whereas average height for both diPEHN and triPEON doped PETN is around 4.5 nm. This is a significant increase of step height because of the presence of doping compound. However it is not possible to explain the mechanism of the increase of step height from this study. Adsorption of doping compounds, which are bigger molecule compared to PETN at the edge of the growth layers might increase the height of the growth layer. TriPEON doped PETN crystal exhibited a more random stacking of growth layers compared to the pure one. The growth layers of triPEON doped crystal overlap extensively. AFM images also showed that the edges of layers in both diPEHN and triPEON doped PETN crystals are not as smooth as those in pure crystal and are more disordered pattern. It is a prominent feature in the diPEHN doped crystal. Changes of the edge morphology of the doped crystal may be attributed to the incorporation of the homolog dopant at the edge/kink sites, which is consistent with the previous work presented in literature [20, 21]. Sublimation of PETN is associated with shrinking of the edges [22]. The presence of impurities on the edges might be slowing the shrinkage of the edge, thereby slowing down the overall sublimation rate.

4 Conclusions

A systematic study of the mass-loss rates from single crystals of pure PETN were carried out, and those doped with various amounts of PETN-homologs diPEHN and triPEON at elevated temperatures of 105–125 °C. Our investigation shows that diPEHN and triPEON doping in PETN can reduce the mass-loss rate by as much as 35 % as compared to pure PETN. Arrhenius plots of the TGA mass-loss data show that homolog-doping at any concentration does not significantly change the activation energy barrier of the desorption process, while AFM images provide evidence to the change of roughness on the edge of the growth steps and the stacking of growth layers due to the presence of impurity molecules. While this altered morphology leads to lower mass-loss rates in the presence of the impurity, removal of the impurity with gentle ethanol washing leads to mass-loss rates as much as 80 % higher as compared to pure PETN. From these results we conclude that homolog doping of PETN involves a complex process, including the distribution of impurities both in the bulk material and on the surface, as well as possible segregation of excess impurities outside the PETN crystals. Since the rates of sublimation do not show any clear trend of increase or decrease with temperature, one could possibly extrapolate the above results to room temperature, from which one would conclude that either diPEHN or triPEON doping should increase the stability of PETN powder against coarsening under ambient conditions.

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