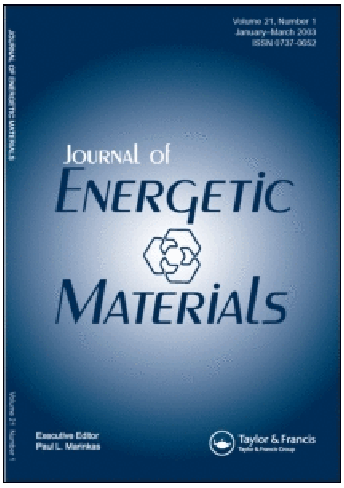

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Effect of Impurity Doping on the Morphology of Pentaerythritol Tetranitrate Crystals

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Pentaerythritol tetranitrate (PETN) is a very powerful explosive and is generally used in initiators. Changes in the morphology and surface area of aging powders are observed during long term storage, due to coarsening mechanisms (e.g., Ostwald ripening, sintering, sublimation, etc.) These changes in powder properties modify the initiation ability and performance. Various stabilization techniques have been investigated to minimize coarsening in PETN powders. In this report we present our study of changes in morphology between the pure PETN and PETN doped with the ions of iron, calcium, sodium, and zinc. We also carried out studies on the effect of

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annealing on the morphology of these crystals at the macroscopic and microscopic levels to determine how the different ions modify the crystal.

Keywords: atomic force microscopy, pure and doped PETN

Introduction

Pentaerythritol tetranitrate (PETN) is primarily used as an initiator for other secondary explosives. For successful applications, the surface area, and density, of PETN should be controlled over extended periods. However with time, the PETN powders change in morphology and surface through coarsening mechanisms (e.g., Ostwald ripening and surface diffusion) [1]. Several external and internal factors are known to affect the crystal growth rate and crystal morphology. Internal factors are defined as the crystal structure, dislocation, and other defects in the crystal and the external factors are those imposed on the crystal by the crystallization conditions defined by growth parameters (temperature, supersaturation, etc.) and introduction of impurities. These internal and external factors can control the growth processes as well as the aging processes of PETN. In order to alleviate the sublimation of PETN crystals, doping with certain impurities during the crystallization of PETN has been proposed.

There have been numerous reviews on the effects of impurities on crystal structure, crystal growth, and the mechanisms of adsorption of impurities [2–9] as well as crystal habit and on crystal growth [2–5]. Others have shown that by adding specific impurities, the morphology and the habit of the crystal can be engineered, or tailor-made [6,7], and attempts were made to model the morphology of organic crystals in the presence of the impurities [8,9]. A systematic study of the change in the crystal structure of sodium chlorate ($NaClO_3$) crystals by addition of various dyes (impurities) was carried out by Buckley [10], and he found a change from cuboid morphology to tetrahedral morphology at different levels of impurity contents. Ristic et al. [11] have studied the effect of sodium dithionate impurity on the morphology of $NaClO_3$ crystals using optical reflection and transmission microscopes. They also studied the effect of cooling rate on the habit of $NaClO_3$ crystal grown from pure solution. They found the morphology of the pure crystal at different cooling rates is cuboid modified by {110} and {111} faces in the low cooling rate (0.007−0.03 K/day) and pure {100} cuboid in the higher cooling rate (0.04–2.0 K/day). At all cooling rates, they found that all natural faces of the crystal are flat faces. The cuboid habit observed for crystal grown from pure solution changes into a tetrahedral habit with the introduction of sodium dithionate impurity.

There have been many studies on the characterization of crystal surface structure at the nanometer scale by atomic force microscopy (AFM) [12–14]. Gratz and Hillner studied the effect of adding phosphates and phosponates on calcite growth [12]. The crystal was grown in situ within the AFM where the effect of the impurity could be directly investigated on the nanoscale. The impurities chosen were industrial inhibitors like HEDP (1-hydroxyethylidene-1,1-diphosphonic acid), NaTP (sodium triphosphate), SHMP (sodium hexametaphophate) with that of natural poisons ($H_nPO_4{}^{3-n}$orthophosphate ions and Mg^{2+} ions). They observed for inorganic phosphates the adsorption is directly at the step edges. When the poisoned surface is again flushed in the supersaturated growth solution, growth is blocked until the existing steps are removed or ‘‘depoisoned.’’ Once regrowth begins, it starts between the poisoned steps until the poisoned regions are buried. Burnham et al. [15] have investigated the surface morphologies {110} plane of pure PETN crystals in the temperature range 22–50°C using in situ AFM at ambient pressure in an open environment. They observed the changes in the surface (island shrinkages and pit growths) as a function of time and determined the activation energy from the step velocities calculated from the observed island shrinkages and pit growths as a function of time.

There have not been many papers dealing with the impurity effect on thermal stability of the PETN crystals [16,17] to date. The impurities investigated in this work were Fe, Ca, Na, and Zn nitrate salts. These metal ions were chosen since they are commonly found in tap water. The production of high-surface-area PETN is often accomplished by crash precipitation of saturated PETN liquor into water. Therefore, impurities in the water can contribute to the overall morphology. Previous studies have determined the activation energy of PETN with these impurities at temperatures above 100°C [17]. In this report we will investigate the qualitative effect of the impurity on the stability of PETN. The impurity-doped crystals will be annealed at temperatures up to 80°C where optical microscopy and atomic force microscopy (AFM) will be used to observe the macroscale and nanoscale morphology, respectively.

Experimental

All PETN crystals were produced by using a solvent evaporation technique. The PETN powder was supplied by Lawrence Livermore National Laboratory, Livermore, CA, USA. A PETN solution was prepared by dissolving the PETN powder in acetone to make a supersaturated solution. For preparing the doped PETN crystals, granules of $Ca(NO_3)_2\ 4H_2O$ (MCB Manufacturing Chemists Inc., Cincinnati, Ohio), $Na(NO_3)$ (Mallinckrodt Inc., Paris, Kentucky), $Fe(NO_3)_3\ 9H_2O$ (J.T. Baker Chemical Co., Phillipsburg, New Jersey), and $Zn(NO_3)_2\ 6H_2O$ (Mallinckrodt Baker Inc., Phillipsburg, New Jersey) were dissolved in acetone in separate vials and PETN powder was dissolved in the each of these solution so that the impurity concentration in the final solution was 100 ppm. All the doped PETN crystals were grown at room temperature.

The optical images were taken by an Olympus SZH stereomicroscope. In the preliminary studies, the crystals were heated and then optical images were taken to see any changes on the top face {110} of the crystal. The crystals were heated from 40 to 80°C in steps of 10°C. There were no changes observed with optical microscopy even after the crystals were heated at 70°C for several weeks. At 80°C, significant changes in the optical image could be observed within a week. For nanoscale measurements, AFM studies were carried out after the crystals were heated at 80°C for an hour and allowed to cool back to room temperature. The AFM images (in contact mode) were taken with a Nanoscope IIIa (VEECO multimode AFM) instrument.

Results and Discussion

Figure 1 shows representative optical images of pure PETN crystal and of doped PETN crystals grown at room temperature. The optical images of room temperature-grown Fe-, Ca-, and Na-doped PETN crystals look similar to that of pure PETN (Figs. 1a, 1c, 1d, and 1e). The top face {110} of the all room temperature-grown doped crystals, except Zn ion-doped crystal, is flat and smooth, similar to that of pure PETN. The Zn-doped PETN crystal differs from the pure as well as other doped crystals (Fig. 1b). Previous thermogravimetric analysis of RT-grown doped PETN crystals showed that Zn-doped PETN grown at room temperature have not only a change in morphology compared to that of pure PETN but also a change in the activation energy for evaporation [17].

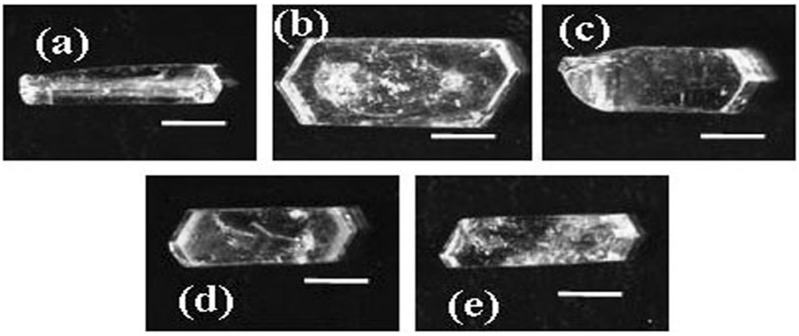

Figure 1. Optical images of crystal of (a) RT-grown Zn-doped, (b) RT-grown Fe-doped, (c) pure, (d) RT-grown Ca-doped, and (e) RT-grown Na-doped PETN. (All scale bars are 2 mm.)

Figure 2 shows the optical images and AFM images of pure, Fe-doped, and Zn-doped PETN crystals before and after annealing at 80°C. For the optical images the annealing time was one week and for AFM images the annealing time was an hour. For Na-doped and Ca-doped crystals there are no significant changes when compared to the pure PETN annealing and these are not shown. The optical images of pure PETN crystals show brighter spots on the top face after annealing (Fig. 2b). The slightly rough areas near the edges of the top face seen at RT seem to smooth out after annealing. The same is observed on the Fe-doped crystals (Fig. 2f). What causes the changes in the structure is not known at this time. Possibilities include surface diffusion, migration of voids or solvent

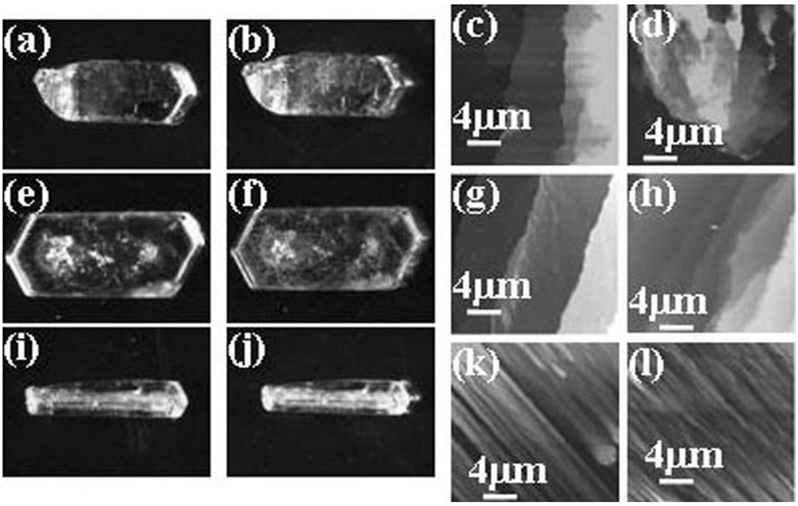

Figure 2. Optical images of (a) pure PETN, (e) Fe-doped PETN, (i) Zn-doped PETN before annealing; and (b) pure PETN, (f) Fe-doped PETN, (j) Zn-doped PETN after annealing at 80°C for a week. AFM images of (c) pure PETN, (g) Fe-doped PETN, (k) Zn-doped PETN before annealing; and (d) pure PETN, (h) Fe-doped PETN, (l) Zn-doped PETN after annealing at 80°C for an hour.

inclusions, and sublimation. However, preliminary studies on the thermogravimetric analysis of pure PETN showed no weight loss on isothermal heating up to 100°C for 24 h [17]. For Zn-doped PETN crystals there is no significant change in the optical images before and after annealing (Figs. 2i and 2j). It should be noted, however, that the morphology of Zn-doped crystals grown at RT is different from that of pure PETN, whereas the Fe-doped PETN crystal grown at RT looks similar to that of pure PETN crystal.

The AFM images on the top face of the pure PETN before annealing show wide and long terraces and the RMS roughnesses measured on these terraces vary around 0.6 and 1.5 nm and the step heights are found to around 15 nm (Fig. 2c). However, RMS roughness measured on the RT-grown Fe-doped PETN crystals ($\sim$2–9 nm) are found to be higher than that of pure PETN and the step heights are found to be varying around 6–100 nm (Fig. 2g). The AFM images of the top face of the RT-grown Zn-doped crystals (Fig. 2k) show a rougher surface (absence of any wide terraces) compared to that of pure PETN with step heights ranging from 5 to 40 nm. The AFM images of Ca-doped and Na-doped PETN crystals (not shown) also indicate rougher surfaces compared to that of pure PETN but have step heights and terraces similar to the pure. In general, the roughness measured on the terraces of the doped PETN crystals is higher than that of pure PETN. The increase in roughness on the surface or on the terraces upon introducing impurities has also been observed by Yoshizaki et al. in the AFM study of doping covalent bound lysozyme dimer (impurity) on hen egg white lysozyme proteins [18]. They found by AFM measurements that {101} and {110} faces of the hen egg white lysozyme protein crystals showed rough surfaces after introducing only 5% of the impurity.

The AFM images on the top face of the pure PETN show that there are significant changes after annealing at 80°C for 1 h (Fig. 2d). The AFM scanning on the top face shows the terraces are not long and wide (as seen before annealing) and the step heights were found to be about 30–50 nm, indicating the bunching of steps. The RMS roughnesses measured on these terraces (less than 2 nm) do not show significant difference compared to that of pure PETN before annealing. The AFM images of Fe-doped PETN crystal after annealing (Fig. 2h) also showed smoother terraces (RMS roughness between 1 and 2 nm) and the terrace widths are smaller prior to annealing. As can be seen from the AFM images of Zn-doped PETN crystals, the surface does not show a significant difference before and after annealing with a constant step height (Fig. 2k and 2l). This result is comparable to the optical images where no changes are observed after heating.

Conclusions

We have shown that the morphology of PETN can be affected on both the macro- and nanoscale by commonly encountered impurities. We have shown qualitatively that Zn impurities may increase the stability of PETN at lower temperatures. Controlling the water-soluble impurities during the production of PETN may yield powders that do not coarsen over time due to better control of the final morphology. When producing the crash precipitation of PETN, the quality of the water should at least be measured so that reproducible results can be obtained with subsequent production lots. Future work will be needed to investigate the long-term thermal and chemical stability, sensitivity, and performance of PETN with these impurities.

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