

PICRIC ACID CRYSTALS RESPONSE TO NANOSCALE MECHANICAL STIMULATION

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Abstract: Reaction of the surface of individual picric acid crystals to the nanoscale mechanical stimulation was studied to understand the processes responsible for the initiation of energetic materials. Three types of the local mechanical stimulation, i. e., nanoindentation, friction, and impact were performed by atomic force microscopy methods. It was found that the stimulation at a nanoscale leads to the disappearance of the material of crystal surface. Moreover, the response to mechanical stimulation differs with crystal faces. In addition, the observed effect slows down with humidity increase probably due to the interaction of the picric acid surface with atmospheric water.

Keywords: atomic-force microscopy (AFM); scanning probe microscopy (SPM); picric acid

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Figure Captions

Figure 1 Face identification of the picric acid crystal

Figure 2 The (010) face and its surface profile with 1-nanometer thick crystal layers

Figure 3 The (–100) face and its surface profile with 2-nanometer thick crystal layers

Figure 4 Picric acid (–100) face morphology after 10 (a), 40 (b), 60 (c), and 90 min (d) after beginning of the investigation

Figure 5 The (–100) face, height profiles showing that due to observed crystal layers rearrangements, sample surface becomes smoother (a) and linear approximation of island (see the circle in Fig. 4b) and hole (see the circle in Fig. 4c) perimeter with time (b)

Figure 6 Results of indentation experiments performed on picric acid crystals: (a) probe indent and particles of extracted materials on (010) face, indentation spot is marked by triangle; (b) and (c) probe indent on (–100) face 10 (b) and 70 min (c) after indentation, marked area indicates the initial size of the indent

Figure 7 Results of the friction stimulation of the picric acid crystals: (a) typical scratch track on the (010) face surface; (b) and (c) hole on the (–100) face surface 6 (b) and 36 min (c) after stimulation, direction of scratching is marked by the dashed line, marked area shows initial size of the hole

Figure 8 The (–100) face, height profiles (a) indicating the disappearance of the material inside the hole which leads to linear volume increase (b)

Figure 9 Results of the impact stimulation of the picric acid crystals; (a) typical notch on the (010) face surface, (b) and (c) increasing hole on the (–100) face surface 10 (b) and 140 min (c) after stimulation, stimulation area is marked by the dashed square

Table Caption

Decrease in the specific growth rate of the scratch track formed on the (–100) face’s surface when exposed to friction, with an increase in humidity

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References

1. Afanas'ev, G. T., and V. K. Bobolev. 1968. *Iniitsirovanie tverdykh vzryvchatykh veshchestv udarom* [Initiation of solid explosives by impact]. Moscow: Nauka. 172 p.
2. Field, J. E., N. K. Bourne, S. J. P. Palmer, S. M. Walleley, J. Sharma, and B. C. Beard. 1992. Hot-spot ignition mechanisms for explosives and propellants [and discussion]. *Philos. T. Roy. Soc. A* 339(1654):269–283.
3. Armstrong, R. W., H. L. Ammon, W. L. Elban, and D. H. Tsai. 2002. Investigation of hot spot characteristics in energetic crystals. *Thermochim. Acta* 384(1-2):303–313. doi: 10.1016/S0040-6031(01)00786-9.
4. Dubovik, A. V. 2011. *Chuvstvitelnost' tverdykh vzryvchatykh sistem k udaru* [Impact sensitivity of solid explosives]. Moscow: RKhTU im. D. I. Mendeleeva. 276 p.
5. Hua, C., P.-J. Zhang, X.-J. Lu, M. Huang, B. Dai, and H. Fu. 2013. Research on the size of defects inside RDX/HMX crystal and shock sensitivity. *Propell. Explos. Pyrot.* 38:775–780. doi: 10.1002/prep.201200200.
6. Yan, Z., W. Liu, C. Zhang, X. Wang, J. Li, Z. Yang, X. Xiang, M. Huang, B. Tan, G. Zhou, W. Liao, Z. Li, L. Li, H. Yan, X. Yuan, and X. Zu. 2016. Quantitative correlation between facets defects of RDX crystals and their laser sensitivity. *J. Hazard. Mater.* 313:103–111. doi: 10.1016/j.jhazmat.2016.03.071.
7. Weeks, B. L., R. K. Weese, and J. M. Zaug. 2002. Energetic materials and atomic force microscopy: Structure and kinetics. *12th Detonation Symposium (International)*. San Diego, CA. 10 p.
8. Tian, Q., G. Yan, G. Sun, Ch. Huang, L. Xie, B. Chen, M. Huang, H. Li, Y. Liu, and J. Wang. 2013. Thermally induced damage in hexanitrohexaazaisowurtzitane. *Cent. Eur. J. Energ. Mat.* 10(2):359–369.
9. Burnham, A. K., S. R. Qiu, R. Pitchimani, and B. L. Weeks. 2009. Comparison of kinetic and thermodynamic parameters of single crystal pentaerythritol tetranitrate using atomic force microscopy and thermogravimetric analysis: Implications on coarsening mechanisms. *J. Appl. Phys.* 105:104312. doi: 10.1063/1.3129504.
10. Burch, A. C., D. Y. John, and D. F. Bahr. 2017. Nanoin-dentation of HMX and idoxuridine to determine mechanical similarity. *Crystals* 7(11):335–344. doi: 10.3390/cryst7110335.
11. Kovalev, A., and H. Sturm. 2011. Observation of nanoscale hot-spot generation on a 2, 4, 6-trinitrophenol (TNP) single crystal. *Surf. Sci.* 605(17-18):1747–1753. doi: 10.1016/j.susc.2011.06.012.
12. Khabarov, Y. G., A. A. Patrakeev, V. A. Veshnyakov, D. S. Kosyakov, N. V. Ul'yanovskii and A. Yu. Garkotin. 2017. one-step synthesis of picric acid from phenol. *Org. Prep. Proced. Int.* 49(2):178–181. doi: 10.1080/00304948.2017.1291008.
13. Muravyev, N. V., K. A. Monogarov, I. N. Melnikov, A. N. Pivkina, V. G. Kiselev. 2021. Learning to fly: Thermochemistry of energetic materials by modified thermogravimetric analysis and highly accurate quantum chemical calculations. *Phys. Chem. Chem. Phys.* 23(29):15522–15542. doi: 10.1039/D1CP02201F.
14. Fried, L. E., M. R. Manaa, P. F. Pagoria, and R. L. Simpson. 2001. Design and synthesis of energetic materials. *Annu. Rev. Mater. Res.* 31(1):291–321. doi: 10.1146/annurev.matsci.31.1.291.
15. Anczykowski, B., B. Gotsmann, H. Fuchs, J. P. Cleveland, and V. B. Elings. 1999. How to measure energy dissipation in dynamic mode atomic force microscopy. *Appl. Surf. Sci.* 140(3-4):376–382. doi: 10.1016/S0169-4332(98)00558-3.
16. Orlova, E. Yu. 1981. *Khimiya i tekhnologiya brizantnykh vzryvchatykh veshchestv* [Chemistry and technology of high explosives]. Leningrad: Khimiya. 312 p.
17. Boldyrev, V. V. 1983. *Eksperimental'nye metody v mekhanokhimii tverdykh neorganicheskikh veshchestv* [Experimental methods in the mechanochemistry of solid inorganic substances]. Novosibirsk: Nauka. 65 p.

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