ISSN 1062-8738, Bulletin of the Russian Academy of Sciences: Physics, 2023, Vol. 87, No. 5, pp. 622–625. © Allerton Press, Inc., 2023.
Russian Text © The Author(s), 2023, published in Izvestiya Rossiiskoi Akademii Nauk, Seriya Fizicheskaya, 2023, Vol. 87, No. 5, pp. 703–707.

Using Synchrotron Radiation to Study the Effect of Irradiation on the Thermal Transformation of Hexaaminonitrowurtzitane Crystals

M. A. Mikhailenko[a, *], M. R. Sharafutdinov[a, b], K. B. Gerasimov[a], E. V. Artemova[a, c], P. I. Kalmykov[c], M. V. Korobeinikov[d], B. P. Tolochko[a, d], and P. A. Piminov[b, d]

[a] *Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630128 Russia*

[b] *Siberian Ring Photon Source Resource Center, Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630559 Russia*

[c] *Altai Federal Research and Production Center, Biysk, 659322 Russia*

[d] *Budker Institute of Nuclear Physics, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*

**e-mail: mikhailenko@solid.nsc.ru*

Received November 28, 2022; revised December 15, 2022; accepted January 25, 2023

Abstract—Small-angle scattering of synchrotron radiation is used to study thermal transformations of ε-form hexanitrohexaazaisowurtzitane crystals subjected to electron beam processing. It is shown the destruction of crystals treated with an electron beam begins far below the point of the polymorphic transition. A conclusion is drawn about the effect products of radiolysis have on the destruction of the crystals. A mechanism of crystal destruction is proposed.

DOI: 10.3103/S106287382270174X

INTRODUCTION

Hexanitrohexaazaisowurtzitane (HNIW) was first obtained in 1987. It is an energy-rich compound with properties superior to those of known analogs in the class of polycyclic nitramines. In recent years, there have been numerous studies on optimizing means of production, reproducible crystallization, resistance to various environmental factors, improving resistance to detonation by synthesizing mixed crystals, and crystalline forms and pseudo-polymorphic modifications (the best known of these are the α-, β-, γ- and ε-forms; the so-called α-form is solvate with water). The ε-form is the one most stable at room temperature. Under standard conditions, it transitions to the γ-form at temperatures of 160–190°C [3]. The change occurs with a slight increase in volume and the rearrangement of intermolecular bonds. If hydrogen bonds are present in all directions in the ε-form, they form layers of HNIW molecules in the γ-form structure.

Small-angle X-ray scattering (SAXS) on synchrotron radiation is actively used to study fast processes with the participation of high-energy compounds (detonation) [4, 5]. Studies of the microstructural state, with and without the effect temperature has on high-energy compounds, show the effectiveness of, e.g., the effect temperature has on the formation of voids in HMX tablets [6] for structural studies of the pore size distribution in TATB [7], and the evolution of pore sizes during heating of the untreated HNIW [8, 9].

The effect treatment with ionizing radiation has on the properties of energy-saturated compounds has been described in many works, but for we could find no works on microstructural transformations in HNIW after exposure to ionizing radiation.

The aim of this work was to study the thermal behavior of ε-form HNIW crystals after electron beam processing with the small-angle scattering of synchrotron radiation.

EXPERIMENTAL

HNIW was synthesized and recrystallized at the Altai Federal Research and Production Center. The purity was ~99.5%, according to high performance liquid chromatography (HPLC). The crystals were in the ε-form. The fraction of 50–140 μm was used in this work.

Processing with accelerated electrons was done using the ILU-6 pulsed linear accelerator at the Institute of Nuclear Physics. The electron energy was 2.4 MeV, the beam current was 328 mA, and the rate

of pulse repetition was 2–2.5 Hz. Irradiation was done by moving the samples under the accelerator's outlet window in doses of 4–5 J/g (kGy), with interruptions to prevent heating. The doses were 20, 40, and 80 kGy.

The change in color after electron beam treatment was measured via diffuse reflection using an SF-2000 UV spectrophotometer with equipped with a specular and diffuse reflection attachment (LOMO, Russia).

Electron paramagnetic resonance (EPR) spectra were recorded with a Spinscan X spectrometer (Adani, Belarus). The operating frequency was 9.45–9.50 GHz.

The thermal transformations of the initial and processed samples were studied at the VEPP-3 synchrotron radiation station of the Siberian Center for Synchrotron and Terahertz Radiation. The single-coordinate OD-3M detector at the Institute of Nuclear Physics was used to register SAXS, $\lambda = 1.504$ Å. The rate of heating was 10°/min.

Morphology was studied on an SN3400 scanning electron microscope (Hitachi, Japan). Magnetron sputtering was used to coat the samples with layers of gold before each experiment.

Our thermal analytical studies were performed on a STA 449 F/1/1 JUPITER synchronous thermal analyzer (Netzsch, Germany) in an atmosphere of Ar. The rate of heating was 10°/min.

RESULTS AND DISCUSSION

Electron-beam treatment of the ε-form HNIW crystals colored our samples yellow in proportion to the dose of ionizing radiation. Electron spectroscopy of diffuse reflectance (ESDR) revealed a bathochromic shift of the edge of the absorption bands in the treated samples. An untreated sample had a band of ~25300 cm^{-1}. After treatment, there were shifts to ~25100, 24750, and 24300 cm^{-1} at doses of 20, 40, and 80 kGy, respectively. The intensity of absorption also rose in the region of 19000 cm^{-1}, a band observed in the initial sample and probably caused by impurities in the crystals.

To measure the change in the intensity of SAXS during heating, we used samples of the initial HNIW crystals 1–2 days after they were treated with doses of 20 and 80 kGy, along with crystals treated with a dose of 40 kGy and stored for 1 year. Figure 1 shows the curves of changes in the intensity of SAXS in the initial and treated samples upon heating.

With the initial HNIW crystals, heating did not cause any notable changes in the scattering pattern up to the start of the $\varepsilon \rightarrow \gamma$ phase transition. With the treated crystals, we can distinguish 3–4 segments on the curves of SAXS intensity:

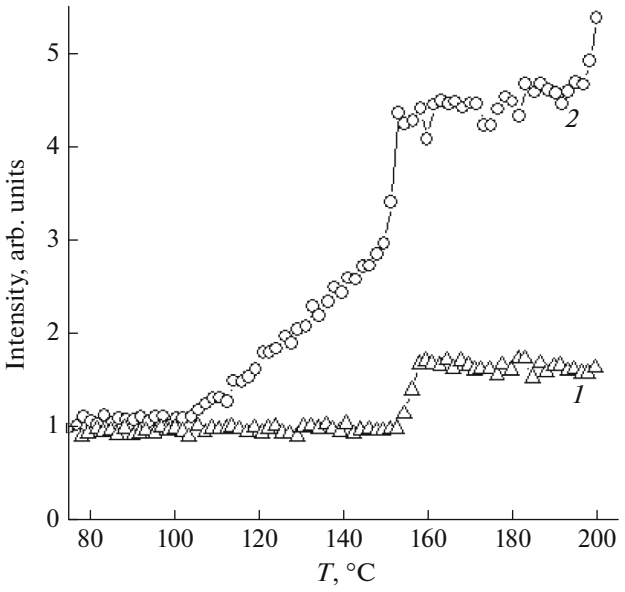

Fig. 1. Change in SAXS intensity during HNIW heating: (*1*) initial sample, (*2*) sample treated with a dose of 40 kGy.

• the range of $T \sim 90$–110°C (depending on the dose of radiation: 90, 100, and 110°C for 20, 40 and 80 kGy, respectively);

• a linear increase in SAXS intensity up to the point of the phase transition, where there is an abrupt rise for samples subjected to long-term storage, and a weak one for those studied shortly after treatment;

• the treated samples next show a linear increase in SAXS intensity up to a temperature of 190–200°C. It is pronounced for samples after doses of 20 and 80 kGy, and negligible for samples that were stored;

• above temperatures of 190–200°C, the treated samples begin active transformations with intense evolution of gas.

The main products of the transformation of energy-saturated compounds upon treatment with ionizing radiation are gases that include nitrogen oxides [10]. In the crystalline phase, they can stabilize on voids in the crystal structure. Electron paramagnetic resonance (EPR) studies of crystals after electron-beam processing show a sharp reduction in the intensity of signals over several hours and the emergence of the stable signal typical of nitroxyl radicals. At the initial stage of sample storage, there was a set of signals of radicals with high mobility (narrow lines), which subsequently changed into one signal with a wider line (low mobility). This effect could be due to the migration of radicals in the structure, which can change the nature of crystal transformation after long-term storage.

Analysis of the structure of different HNIW crystalline modifications showed that with the initial

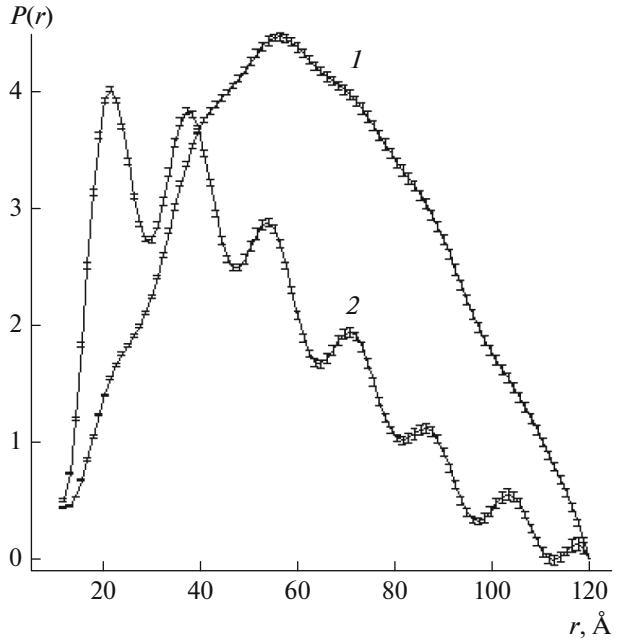

Fig. 2. Pore size distribution for an HNIW sample treated with a dose of 80 kGy at different temperatures: (*1*) 100, (*2*) 180°C.

ε-form, the dissolution of gases in it (including NO_2) is not energetically advantageous [11, 12]. Even negligible amounts of nitrogen oxides should cause an increase in stresses. This explains the onset of the treated crystals' destruction at lower temperatures and the temperature's dependence on the dose at the start of the process.

Our data were processed according to several models [13]. The criteria for the models' applicability were the correspondence of the expected scattering curves to the experimental data in the selected range of radii r_{max}, and the positive nature of scattering function $P(r)$. For crystals treated with an electron beam, the scattering curves obtained at different temperatures were described according to different models. Up to the temperature of the ε–γ transition, the best model was the spherical one used in [9]. After the polymorphic transformation, the rods model was better.

Figure 2 shows diagrams of the $P(r)$–r scattering function for a sample treated with a dose of 80 kGy at different temperatures.

The $P(r)$–r curve obtained at 100°C is a combination of several Gaussian distributions according to the spherical model. The choice of the rods model when processing data obtained at a temperature of 180°C gave similar results. This model could correspond to the development of the predominant micro(nano)cracks.

Our study of the samples' morphology after thermal treatment confirms this assumption. Figure 3 shows electron microscope images of HNIW crystals after 30 min of exposure at 170°C.

With untreated HNIW crystals, the shape of the initial ε-phase crystals (particles 50–140 μm in size with a small number of smaller irregular particles) is retained with pronounced predominant cleavage along plane *xy* (indicated by the initial crystals) and, to a much lesser extent, in the plane perpendicular to it. The influence of the electron-beam results in greater destruction of crystals when heated (the formation of irregularly shaped particles no larger than 40–50 μm in size).

However, the tendency for cracking in the form of parallel cracks remains, due to layers associated with

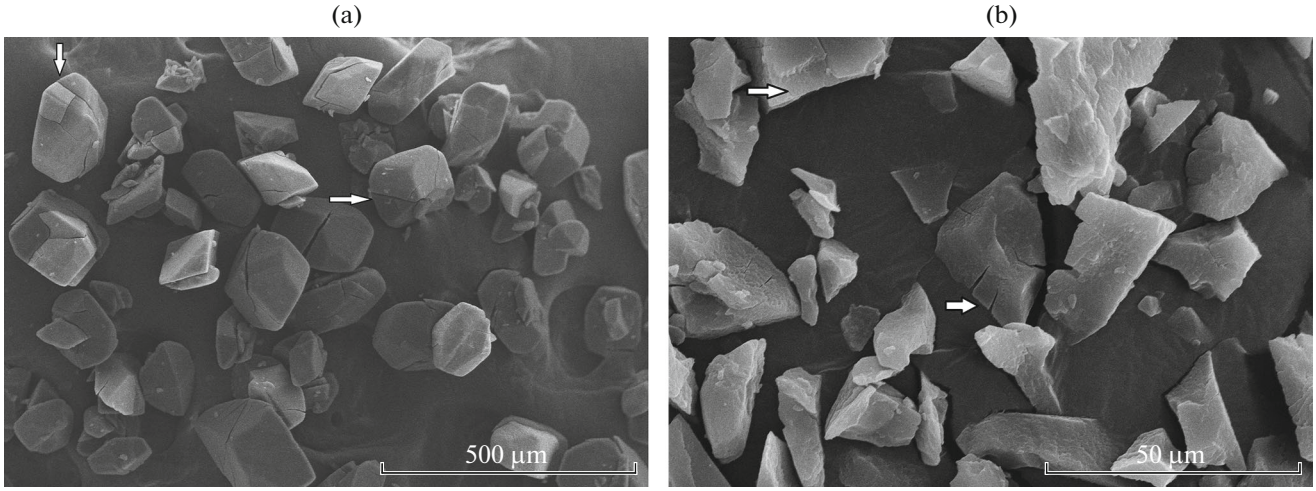

Fig. 3. Electron micrographs of HNIW samples after heat treatment: (a) initial, (b) treated with a dose of 80 kGy.

the van der Waals interactions. This causes planes of cleavage along which mechanical stresses relax.

FUNDING

This work was performed on equipment at the Siberian Center for Synchrotron and Tetrahertz Radiation based on the Institute of Nuclear Physics' VEPP-4–VEPP-2000 electron–positron collider complex with the support from the RF Ministry of Science and Higher Education, project no. FWUS-2022-0001.

REFERENCES

1. Nielsen, A.T., Chaén, A.P., Christian, S.L., et al., *Tetrahedron*, 1998, vol. 54, no. 39, p. 11793.
2. Sysolyatin, S.V., Lobanova, A.A., Chernikova, Yu.T., et al., *Russ. Chem. Rev.*, 2005, vol. 74, no. 8, p. 757.
3. Russell, T.P., Miller, P.J., Piermarini, G.J., et al., *J. Phys. Chem.*, 1993, vol. 97, no. 9, p. 1993.
4. Titov, V.M., Pruuel, E.R., Ten, K.A., et al., *Combust., Explosion. Shock Waves*, 2011, vol. 47, p. 615.
5. Aleshaev, A.N., Zubkov, P.I., Kulipanov, G.N., et al., *Combust., Explosion. Shock Waves*, 2001, vol. 37, no. 5, p. 585.
6. Guanyun, Y., Qiang, T., Jiahui, L., et al., *Cent. Eur. J. Energ. Mater.*, 2016, vol. 13, no. 4, p. 916.
7. Smirnov, E.B., Muzyrya, A.K., Kostitsyn, O.V., et al., *Bull. Russ. Acad. Sci.: Phys.*, 2015, vol. 79, no. 1, p. 20.
8. Wang, H., Xu, J., Sun, Sh., et al., *Molecules*, 2020, vol. 25, no. 3, p. 443.
9. Zhang, H., Wang, H., Xu, J., et al., *Materials*, 2022, vol. 15, no. 12, p. 4258.
10. Kim, Yu. and Ponomarev, A.V., *Mendeleev Commun.*, 2020, vol. 30, no. 4, p. 531.
11. Beste, A. and Kathleen, M., *Propellants, Explos., Pyrotech.*, 2022, vol. 47, no. 5, p. e202100359.
12. Beste, A., *Propellants, Explos., Pyrotech.*, 2022, vol. 47, no. 5, p. e202100360.
13. Semenyuk, A.V. and Svergun, D.I., *J. Appl. Crystallogr.*, 1991, vol. 24, no. 5, p. 537.
14. Shim, H.-M. and Koo, K.-K., *Cryst. Growth Des.*, 2016, vol. 16, no. 11, p. 6506.

Translated by E. Domoroshchina