LA-UR- 99-3397

Approved for public release; distribution is unlimited.

Title: SOME OBSERVATIONS ON THE STRUCTURE OF TATB

Author(s): D.S. Phillips
R. B. Schwarz
C. B. Skidmore
M. A. Hiskey
S. F. Son

Submitted to: AIP meeting, Shock Compression of Condensed Matter
Snowbird, UT
June 28-July 7, 1999

Los Alamos
NATIONAL LABORATORY

DISCLAIMER

Some Observations on the Structure of TATB

D.S. Phillips, R.B. Schwarz, C.B. Skidmore, M.A. Hiskey, and S.F. Son

Los Alamos National Laboratory

The recent discovery of second-harmonic light generation (SHG) from 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) has renewed interest in both the crystallography and the identification of defect structures in this material. The accepted crystal structure is triclinic but centrosymmetric (P-1); SHG is not expected from materials of this symmetry. A wide variety of syntheses have been shown to produce SHG-positive materials, including an emulsion technique, two different recrystallization methods, and a variety of combined reaction - precipitation processes. In addition, two standard commercial powders have shown the property after annealing in the 300 C range. We have examined the structures of several of these powders using polarized light microscopy (PLM), scanning electron microscopy (SEM), and powder X-ray diffraction (XRD). We find that SHG-positive materials typically contain crystals both more transparent and more strongly faceted (i.e. "more perfect") than weak-SHG ones and that the positive samples show stronger texture in their powder diffraction patterns. These results are compared with predictions from Cady's structure.

INTRODUCTION:

The structure of TAB was determined by Cady and Larson[1] to consist of planar molecules, hydrogen bonded into sheets, and stacked on a triclinic but centrosymmetric lattice (P-1). Disorder in the stacking of these sheets is common, often resulting in twins, and perfect crystals are rare.

In the thirty years since the first structure determination, several studies have elaborated on that structure. Kolb and Rizzo[2] measured the temperature dependence of the lattice parameters of several crystals and reported a minority monoclinic phase in addition to the received triclinic one. Voigt-Martin et al[3] performed selected area electron diffraction on thin crystals recrystallized from dimethylsulfoxide onto TEM grids and identified another minority phase with a large hexagonal unit cell.

The report of laser frequency doubling or second harmonic generation has cast further doubt on our understanding of the TATB structure [3-6]. This physical property is formally forbidden in centrosymmetric crystals, leading to speculation that it arises from surface regions of relaxed symmetry, from crystal defects (esp. twins), form the dynamic polarization of the lattice away from its equilibrium structure under the intense electric field of the exciting laser beam, or from the thermal libration of molecules or intramolecular groups away from their average positions.

Son et al[6] have shown that several distinct TATB preparations perform very differently (by a factor of 10^4) in SHG and that some annealed or novel samples are among the most efficient doubling crystals known. The aim of the present work is to evaluate the structures of several of these SHG-diverse TATB's from the lattice to millimeter scales and identify the structural features most typically associated with the presence or absence of SHG.

EXPERIMENTAL:

Both dry-aminated and wet-aminated commercial powders were examined as received and after annealing at 300 C in air on a hotplate. In addition "ultra fine" commercial milled powder was examined as received and likewise annealed.

Material was purified from dry-aminated commercial powder by several recrystallization schemes using either nitrobenzene, diphenyl ether, or dimethy sulfoxide as solvent. At ~ 1 w/o concentrations, the temperatures at which these solutions cool to saturation differ widely, from 180 C for nitrobenzene to 80 C for DMSO. A significant amount of material precipitated from the DMSO solution at temperatures below 60 C.

Samples were prepared for microscopic observation by either mounting in Cargille index media (n=1.660) for examination in transmitted polarized light or by sprinkling on a

carbon sticky tab and coating with ~ 10 nm of sputtered gold for SEM.

Powder X-ray diffraction was performed on selected samples using a Rigaku rotating anode generator in vertical θ/θ geometry and dispersing the powder on a "zero background" quartz plate. Results were analyzed using GSAS[7].

Samples for examination in TEM were prepared by ultrasonic dispersion of fine recrystallized powders in acetone and dipping holey carbon films to pick up the particles. These were examined in a Philips CM30 microscope operated at 100 kV with a sample temperature of ~ 20 K.

RESULTS:

The SHG efficiency of several diverse TATB materials was qualitatively evaluated by the method of Son et al[6], as shown in Table 1.

Table 1. SHG Efficiencies of Various TATBs

Low efficiency	Dry aminated commercial
	Wet aminated commercial
	Ultrafine commercial
	Ultrafine precipitate
High efficiency	Annealed dry aminated
	Annealed wet aminated
	Annealed ultrafine
	All recrystallized powders
	All ultrasonic powders

Figures 1 and 2 show typical SEM views of dry-aminated production powder before and after 300 C annealing respectively. The as-received powder is remarkably uniform in particle size, though it is clear that the granule shown contains numerous crystallites. The density of voids or "worm holes" is striking, as is their regular, ~ 1 μm diameter. This material is "SHG negative".

In contrast, figure 2 shows a great deal of anisotropic grain growth, accompanyed by a remarkably reduced density of somewhat coarsened worm holes. It can be argued that the 30 micron aggregate now consists of only a few distinctly oriented crystals based on the symmetry of the surviving growth steps. This material is "SHG positive".

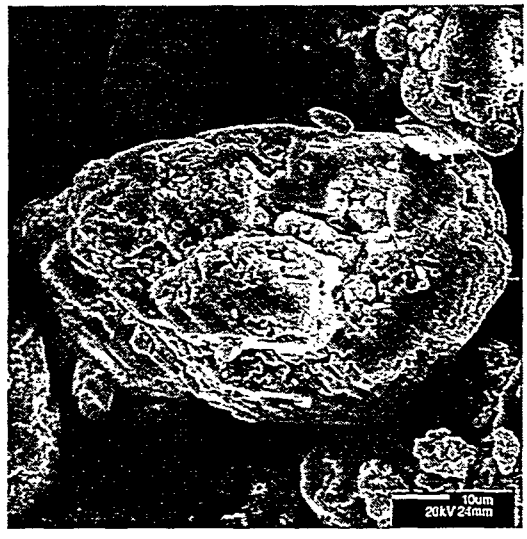

Figure 1. Dry aminated commercial powder, as received

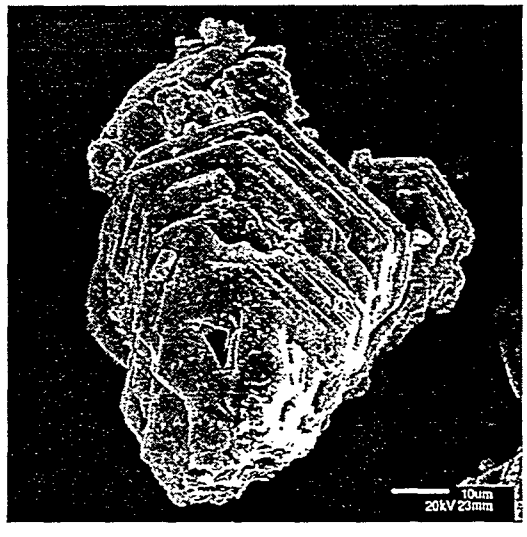

Figure 2. Dry aminated commercial powder, annealed

Figure 3 shows a SHG negative ultrafine powder as received. This material is known to be derived from commercial powders by severe milling. The structure shown in figure 3 is entirely consistent with such a heritage. Note that the particles are distinctly platelike in morphology and range from submicron to several micron apparent diameters. The platelets appear to be quite fine and often agglomerated, though still on a much finer scale than the 30 micron commercial starting powders. The particles appear to be dense, though they are sufficiently thin to be penetrable by the 20 kV electron beam.

Figure 3. "Ultrafine" commercial powder

Figure 4. Commercial powder recrystallized from nitrobenzene

Figure 4 shows dry aminated commercial powder recrystallized by dissolution in boiling nitrobenzene and hot filtration of the product at 160 C. Particles of two morphologies are apparent – very broad thin plates and smaller compact faceted crystals. Both particles appear to be single crystals, though the coarse plates often contain subgrain boundaries and occluded solvents.

DISCUSSION:

We hypothesize from these observations that the prerequisites for SHG positive TATB are the following:

> Crystallites larger than a micron,
> Free of micron-range wormholes.

We suppose that these requirements serve to mitigate the attenuation of the incident laser beam by interfacial scattering. This should be particularly intense in TATB, a biaxial crystal of exceptional birefringence. Cady determined $X = 1.45$ and estimated $Y \sim 2.3$ and $Z \sim 3.1$ [8]. Consequently both crystal to air and crystal to (differently oriented) crystal interfaces should be potent scatterers, especially when the sizes of the scatterers approach the wavelength of the excitation.

In this scenario, TATB crystals would be intrinsically SHG positive. This could arise from crystal defects, though the increase in response on annealing out the worm holes makes surface activity seem unlikely. We have not yet tracked the evolution of twin and stacking fault structures through the annealing and solvent recrystallization processes, though some such experiments have been planned. It is worth noting that high densities of twins (recurring stacking errors) have been reported since the earliest structural studies of TATB[8].

It is also conceivable that defect free TATB could be SHG positive. The apparent symmetry of the TATB molecule is –6m2 or D_{3h}. *This idealized symmetry is still consistent with the presence of SHG*[4]. It is normal that the forces giving rise to solid cohesion degrade this symmetry, first by the introduction of hydrogen bonds among the molecules within a sheet, then by Van der Waal's interactions among sheets, and finally by thermal motion. These perturbations within the molecule remove – not add – symmetry elements and can't be argued to disallow the process. Perhaps the most unusual aspect of the structure of TATB, however, is that it chooses a stacking sequence which *does add* an inversion center not intrinsic to either the molecule or its hydrogen bonded layers. This third-order structure and bonding effect is not consistent with the presence of SHG and motivates the current discussion.

ACKNOWLEDGMENTS:

This work is sponsored by the U.S. Department of Energy under contract number W-7405-ENG-36. The authors wish to thank Phil Howe for fiscal and philosophical support, Mike Coburn and Don Ott for providing archival samples, and especially Howard Cady for most helpful discussions.

REFERENCES:

1. H.H. Cady and A.C. Larson, The Crystal Structure of 1,3,5-Triamino-2,4,6-trinitrobenzene", Acta Cryst. (1965) 18, 485.

2. J.R. Kolb and H.F. Rizzo, "Growth of 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB), I. Anisotropic Thermal Expansion", Propellants and Explosives 4, 10-16 (1979).

3. I.G. Voigt-Martin, G. Li, A.A. Yakimanski, J.J. Wolff, and H. Gross, "Use of Electron Diffraction and High-Resolution Imaging to Explain Why the Non-dipolar 1,3,5-Triamino-2,4,6-trinitrobenze Displays Strong Powder Second Harmonic Generation Efficiency", J. Phys. Chem. A 1997, 101 7265-7276.

4. J. Zyss and I. Ledoux, "Nonlinear Optics in Multipolar Media: Theory and Experiments", Chem. Rev. 94, 77-105 (1994) reviews early work on TATB.

5. G. Filippini and A. Gavezzotti, "The crystal structure of 1.3.5-triamino-2,4,6-trinitrobenzene. Centrosymmetric or non-centrosymmetric?" Chem. Phys. Let. 231 (1994) 86-92.

6. S.F. Son, B.W. Asay, B.F. Henderson, R.K. Sander, A.N. Ali, P.M. Zielinski, D.S. Phillips, R.B. Schwarz and C.B. Skidmore, "Dynamic Observation of a Thermally Activated Structural Change in 1,3,5-Triamino-2,4,6-trinitrobenze by Second-Harmonic Generation" J. Phys. Chem, in press.

7. A.C. Larson and R.B. Von Dreele, "GSAS: General Structure Analysis System", LAUR 86-748 (revised 1997).

8. H.H. Cady, "Crystallographic Data for 1,3,5-Triamino-2,4,6-trinitrobenzene". The Microscope and Crystal Front, 14, 57-58, 1963.