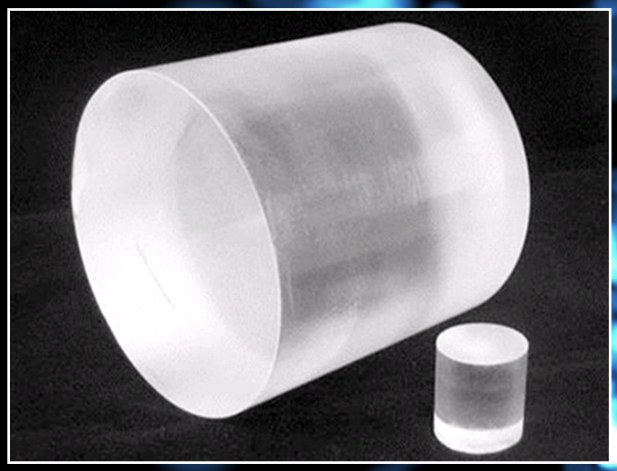
Lawrence Livermore National Laboratory

7000 East Avenue
Livermore CA 94550

Contact
Natalia Zaitseva

Solution-Grown Crystals for High-Energy Neutron Detection



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Solution-Grown Crystals for High-Energy Neutron Detection

1. PRODUCT/SERVICES CATEGORIES

A. Title of Entry

Solution-Grown Crystals for High-Energy Neutron Detection

B. Product Category (Choose one from online list)

Mechanical/Materials

2. R&D 100 PRODUCT/SERVICE DETAILS

A. Name of primary submitting organization

Lawrence Livermore National Laboratory

B. Name(s) of co-developing organization(s) if applicable

Inrad Optics, Inc.

C. Product/service brand name

Solution-Grown Crystals for High-Energy Neutron Detection

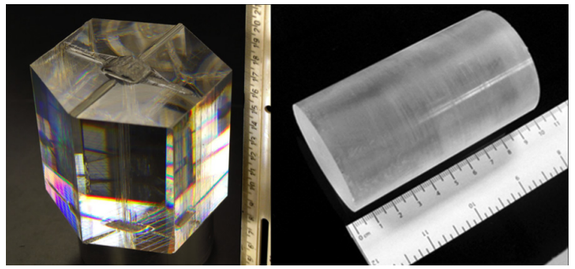

Figure 1. Solution-grown stilbene crystal (left) and a stilbene cylinder (right) shaped from the faceted crystal for use in neutron detection. Stilbene is the first aromatic crystal ever produced by the solution-growth method at commercial scale.

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D. Price of product/service in U.S. Dollars

Crystals are sold in a range of shapes and sizes; the price per cc is not exactly constant. The current cost for a typical 3-in.-by-3-in. cylinder is $20 per cc. With further advances and the emergence of a larger market, the price for a similar-sized cylinder is expected to be further reduced to $8 per cc.

E. Short description of the product (MAXIMUM 25 WORDS)

A solution method developed for growing large-scale, economical stilbene crystals that offer superior capabilities for high-energy neutron detection compared to any other known materials.

3. PRODUCT/SERVICE DESCRIPTION

A. What does the product or technology do?

High-energy and fast neutrons emitted by highly enriched uranium and plutonium produce a signature that is specific to these special nuclear materials (SNM). This neutron signature in particular offers the capability to selectively detect and distinguish SNM from other (non-threat) radioactive sources, which is critical for applications in homeland security and nonproliferation, as well as in scientific research and radiation protection. Crystalline stilbene (diphenylethylene) is a molecular organic crystal built of aromatic hydrocarbon molecules, having the chemical formula $C_{14}H_{12}$. It has long been recognized as having outstanding scintillation properties for detecting high-energy neutrons. In fact, stilbene has the potential to facilitate dramatic improvements in the technologies used for detection and characterization of neutron radiation, with potential applications at nuclear reactors, industrial and research neutron sources, and in equipment designed for identification of special nuclear material for "search" and nonproliferation applications. The first small (about 1-cm size) stilbene crystals were grown more than 50 years ago using melt-growth techniques. However, difficulties in applying these techniques to growing large aromatic crystals led to low yields and size limitations, rendering stilbene unsuitable for significant deployments and widespread adoption in radiation detection. Consequently, liquid scintillators have remained the dominant option for fast neutron detection despite their hazardous nature and inferior properties. Conventional solution-growth methods were not applied to stilbene because, traditionally, such methods were used only for producing water-soluble inorganic crystals. The technology developed at LLNL enables application of the solution-growth method to a large class of

new materials that can be grown from alternative organic solvents, opening further opportunities for exploration of properties and potential application of new organic materials. The method demonstrates an easy, scalable, economical route for growing large numbers of crystals in many sizes. Stilbene became the first pure aromatic crystal ever produced at large scale (>10 cm) by the solution-growth method. Our technology has been adopted by Inrad Optics for commercial production, making the replacement of less-efficient and hazardous liquid scintillators with superior, solid-state stilbene now possible and available for widespread use in radiation detection.

B. How does the product operate?

Detection of high-energy neutrons in the presence of background gamma radiation utilizes the difference in the shapes of the scintillation (fluorescence) pulses excited by neutrons and gamma rays in stilbene crystals. The technique, pulse shape discrimination (PSD), is based on the existence of two-decay component fluorescence, in which, in addition to the main component decaying exponentially (prompt fluorescence), there is usually a slower emission that has the same wavelength but longer decay time (delayed emission). The fast component results from the direct radiative emission of excited singlet states, while the slow component originates from the collisional interaction of pairs of excited molecules in the lowest excited triplet states. A high concentration of hydrogen in the aromatic rings of stilbene provides conditions for neutron interaction and efficient fluorescence. The short range of the energetic protons produced from neutron collisions with hydrogen yields a high concentration of triplets compared to the longer range of the electrons from the gamma interactions, leading to the enhanced level of delayed emission with longer decay times in neutron-induced pulses in comparison to those produced by the gamma excitation (see Figure 2b). Using modern high-speed waveform digitizers, neutron and

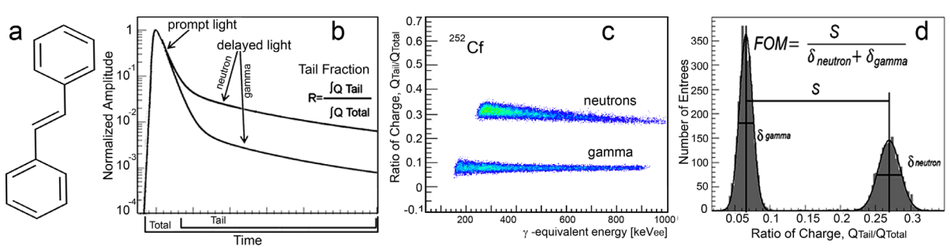

Figure 2. (a) Chemical formula of stilbene. (b) Average waveforms indicating different levels of delayed light in neutron and gamma scintillation pulses; ratio of signal integrals, R, collected in two time gates, Tail and Total, is used for neutron/gamma pulse separation. (c) Typical PSD pattern of a stilbene crystal obtained by digitized separation of neutron and gamma pulses. (d) PSD profiles of experimental data used for calculation of the PSD Figure of Merit (FOM).

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gamma signals can be easily separated based on the fraction of the delayed light in corresponding scintillation pulses (Figure 2c). The quantitative evaluation of PSD in different scintillators is made by calculation of the Figure of Merit (FOM), which is determined by the separation between neutron and gamma distributions and the width of the corresponding peaks (Figure 2d). Since gamma radiation is a ubiquitous background, the ability of stilbene to distinguish neutrons from this background is a critical feature of these types of detectors.

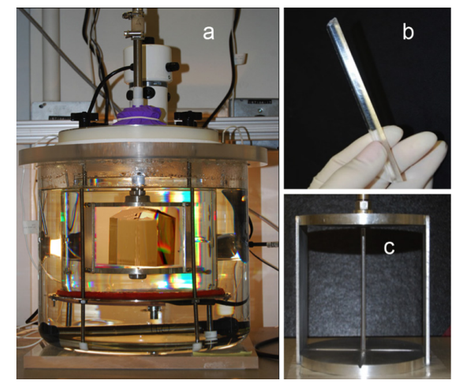

Figure 3. (a) Photo of a solution-growth station designed to produce stilbene crystals; (b) crystals grow from long, thin seeds; (c) seeds are attached to an Al platform.

Our solution-growth process is conducted in double-jar crystallizers, where the inner jar with the solution of stilbene dissolved in the organic solvent (anisole) is placed in an external water bath used for temperature control (see Figure 3a). Special materials resistant to the aggressive organic solvent are used in the design of the crystallizer. All controlling equipment, such as stirrers, heaters, coolers, and thermocouples, are located outside the crystallizer to keep the growth solution in minimum contact with parts of the equipment.

Crystal growth starts from a long, thin seed (Figure 3b) cut along the monoclinic b-axis of stilbene. The seed is glued on an Al platform (Figure 3c) and introduced into the solution. The growth process is controlled by gradual reduction of the solution temperature to maintain the supersaturation, σ, needed to obtain a desired growth rate:

$$\sigma = \left(\frac{PC_0 - M}{C_{0t}(P - M)} - 1 \right) 100\%$$

where P and C_0 are the weight and the equilibrium concentration of the initial growth solution, respectively, and C_{0t} is the equilibrium concentration of the growth solution at the temperature of measurement, t.

4. PRODUCT COMPARISON

A. Supply a matrix or table showing how the key features of your product compare to existing products or technologies. Use numerical figures to represent performance metrics. For price, and capital and operating costs, use actual dollar amounts or a relative scale to show a comparison.

Some key features of Solution-Grown Crystals for High-Energy Neutron Detection are summarized in the following table. Additional comparative detail is provided in Section 4B.

Performance	LLNL Solution-Grown Scintillator Crystals	Commonly Used Liquid Scintillators	Melt-Grown Scintillator Crystals
Light output (in a.u.)[1]	85 to 55	43 to 30	77 to 45
Pulse shape discrimination (PSD)[2]	4 to 3.4	2.9 to 2.5	3.6 to 2.8
Crystal growth rate	20 mm/day	N/A	1 mm/day
Operating temperature (°C)	–40 to 60	5 to 40	–40 to 60
Typical product delivery time	Week to month	Week	Months to year
"Field-ability"	Excellent	Difficult, often not permitted	Excellent

[1] *In increasing scintillator lengths from 0 to 10 cm.*
[2] *Figures of Merit measured at 480 keVee in scintillators ranging from approximately 8 mm to 10 cm in length.*

B. Describe how your product/service improves upon competitive products or technologies.

Comparative studies conducted with crystals of different lengths showed that solution-grown material has light output and PSD characteristics better than either melt-grown stilbene or liquid scintillators (see Figure 4).

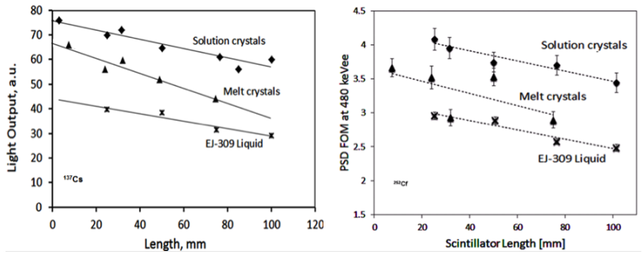

Figure 4. Light output and PSD measured in solution-grown stilbene compared to melt-grown crystals and liquid scintillators.

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The solution-grown stilbene crystals have substantially better scintillation properties because they possess a higher degree of structural perfection than melt-grown crystals (see Figure 5). However, above and beyond the superior detection performance of solution-grown crystals over melt-grown crystals, **the most crucial advantage is ready commercial availability**. Melt-grown stilbene has been produced only in Ukraine (at the Institute of Scintillation Materials) and only in very small quantities at modest size. Thus, melt-grown stilbene is simply not available in sufficient quantities for use in neutron detectors deployed in the U.S. and other countries. By contrast, our commercial partner, Inrad Optics, has successfully adapted our robust solution-growth technology to commercial production of high-quality stilbene crystals within two years after beginning their development effort. Their initial customers have included national laboratories, universities, government, and private industry. These customers have purchased stilbene for testing, with the potential for substantially larger quantities as needed. Approximately $300,000 in stilbene crystals have been sold to-date and customer feedback has been overwhelmingly positive. As stilbene is proven viable for neutron detection in handheld or fixed platforms produced, large quantities are available for homeland security, first responders, and military personnel; we anticipate that stilbene sales could reach $3–10 million per year within a decade. Of course, the complete detector (including packaging, electronics and software), outfitted with the stilbene crystal, could easily cost five times as much.

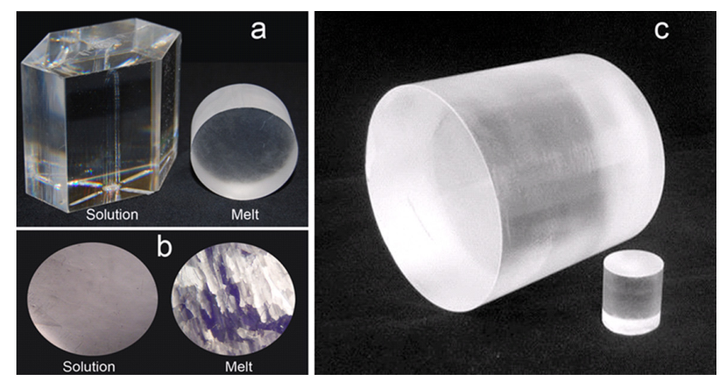
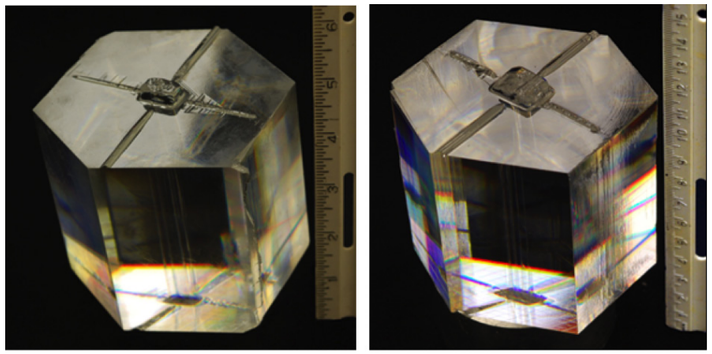


Figure 5. (a) Photographs of solution- and melt-grown stilbene crystals; the height of the solution-grown crystal is 10 cm. (b) Corresponding microscopic images showing the high homogeneity of solution-grown crystals compared to melt-grown crystals, which contain misaligned blocks and grain boundaries. The superior optical transparency of our solution-grown crystals at increasing size is due to the absence of structural defects, which cause light loss and PSD degradation. (c) A large 4-in.-by-4-in. stilbene cylinder commercially produced by Inrad Optics using our solution-growth technology; a 1-in.-by-1-in. small cylinder is shown for comparison.

Referring back to Figure 4, solution-grown stilbene demonstrates an even greater degree of both light output and PSD when compared to commonly used liquid scintillators, enabling unambiguous detection of neutrons in a wider energy range. However, its main advantage compared to toxic and hazardous liquid scintillators is that stilbene is a solid-state material that can be used in many applications where the deployment of liquid scintillators is problematic or prohibitive (e.g., hand-held devices, large-area detectors in public areas, space exploration, or low or high temperatures outside liquid scintillators' 5-to-40-°C operating range).

Work is underway to further decrease the cost of commercial stilbene crystals so that they can economically replace liquid scintillators in other traditional applications, such as large-array radiation detectors and the active interrogation systems being used by Homeland Security. A decrease in cost will be enabled by further advancing the technology to accelerate the growth rate of crystals by more than an order of magnitude. The accelerated growth technology, already demonstrated at LLNL (see Figure 6), is currently being transferred for commercial production to Inrad Optics to produce the next generation of material.



1 mm/day ⟶ 97 days **20 mm/day ⟶ 10 days**

Figure 6. Photographs showing two stilbene crystals grown by the initial slow and recently developed fast solution-growth methods with corresponding growth rates and crystal growth durations. The advanced rapid growth method is being used for stilbene cost reduction. The current commercial growth rate is about 3 mm/day.

C. Describe limitations of your product/service.

As with any single crystal, stilbene requires gentle care, which is not unusual for radiation detectors in general. It is fragile, and can be fractured or broken if dropped. It can also develop cracks if exposed to a sharp temperature change from hot (approximately 30 °C) to freezing (–10 to –20 °C).

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5. SUMMARY (Maximum 175 words)

Protection against nuclear or radiological attack has motivated the search for more definitive radiation detection and identification technologies. Detecting and distinguishing neutrons and gamma rays is key to identifying nuclear substances such as uranium and plutonium and differentiating them from benign radioactive sources. Current detection devices typically employ commercial liquid scintillators, which are inexpensive and readily available but have low resolution and limitations such as toxicity, flammability, and handling difficulties in the field. Solution-Grown Crystals for High-Energy Neutron Detection made of stilbene constitute the best known scintillator material capable of efficiently distinguishing neutrons from gamma rays. These scintillators offer light output and PSD that provides much better resolution than liquid scintillators, but without the associated limitations and hazards. In addition to superior scintillation performance, our solution-grown crystals offer higher quality, easier fabrication, commercial availability, and greater scalability than melt-grown crystals. We envision our new method could lead to widespread use of the new materials for large-volume and low-cost detectors that could aid in the protection of ports, stadiums, airport scanners, nuclear power plants, and other large facilities.

6. CONTACT INFORMATION

Principal investigator from each of the submitting organizations:

Name: Natalia Zaitseva

Title: Supervisor

Organization: Lawrence Livermore National Laboratory

Phone: 925-423-3537

Email: zaitseva1@llnl.gov

Name: Amy Eskilson

Title: President

Organization: Inrad Optics, Inc.,

Phone: 201-767-1910

Email: AEskilson@inradoptics.com

Media and public relations person who will interact with R&D's editors regarding entry material:

Name: Connie L. Pitcock

Title: Marketing and Business Development Associate

Organization: Lawrence Livermore National Laboratory

Phone: 925-422-1072

Email: pitcock1@llnl.gov

Person who will handle banquet arrangements for winners:

Name: Connie L. Pitcock

Title: Marketing and Business Development Associate

Organization: Lawrence Livermore National Laboratory

Phone: 925-422-1072

Email: pitcock1@llnl.gov

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