Crystal Growth and Optical Properties of Organic Crystals for Neutron Scintillators*)

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(Received 31 July 2017 / Accepted 31 October 2017)

This paper presents the study of prospective organic-based materials, trans-stilbene and p-terphenyl, as their potential application for new neutron scintillators. Growth of their single crystals by the self-seeding vertical Bridgman method is reported. And evaluation of grown crystals concerning the composition, optical and luminescence properties, and scintillation performance at room temperature is discussed. Their photo- and radioluminesce spectra were peaking at 388 and 408 nm, their quantum yield was of 52.4% and 79.7%, and the light yield were of 0.89 and 1.80 times higher than that of GS-20 standard, respectively. The scintillation decay times of 8.2 ns (trans-stilbene) and 5.8 ns (p-terphenyl) were observed as well.

Keywords: scintillation crystal, melt growth, organic scintillator, neutron scintillator, self-seeding vertical Bridgman method, optical property

DOI: 10.1585/pfr.13.2405011

1. Introduction

Recently, new applications of neutron scintillators have been developed for imaging methods in a pulsed neutron sources and neutron resonance absorption spectroscopy. These methods require sensitive neutron detectors with the Time-of-Flight (TOF) regime and fast response. In recent years, some of halide scintillators show high light yield and fast decay time, however, most of them are hygroscopic limiting their practical applications. Thus, the organic scintillating crystals showing fast decay time in the nanosecond range and no hygroscopic nature may be suitable alternative. Their constituent elements include hydrogen which shows high reaction cross-section to thermal and fast neutrons [1]. Research of laser-driven directional neutron sources for radiography has been developed. Organic scintillator would be used for TOF technique of this research and heated by neutron repeated irradiation. However, conventional organic scintillators have low melting temperatures which may lead easily to overheating of their melt and subsequent degradation. Therefore, we have developed organic crystals for neutron scintillators with high melting temperatures at least 200°C and fast decay times. For the candidate material research, we prepared for the growth and evaluation system of organic crystals.. As the first step, we grew and evaluated trans-stilbene and p-terphenyl crystals, which have been conventionally used for neutron detection. In particular, the melting temperature of p-terphenyl crystals is over 200°C.

2. Experimental Procedure

Crystal growth was performed by self-seeding vertical Bridgman (SSVB) method [2], as shown in Fig. 1. New design of quartz ampule was composed of the inner ampule and the outer one as a grain selector to support the growth of the single crystal in the inner one. Trans-stilbene (purity 98% up, Tokyo Chemical Industry) and p-terphenyl (purity 99.0% up, Tokyo Chemical Industry) powders were used as starting materials, respectively. Raw powder was loaded into ampule and set in a vacuum chamber, see Fig. 2. The air in the chamber was evacuated and filled with an inert atmosphere of 5 N nitrogen gas. The ampule was heated with a resistive heating until melt occurred and pulled down at the rate of 0.72 mm/h.

After the crystal growth ended, the inner and outer ampules were separated, and the grown crystal in the inner ampule was taken out. The specimens for luminescent property evaluations were prepared by cutting and polishing the grown crystals of 2.3 mm thickness.

The parts of the grown crystals near selected specimens were ground into powders and used for powder X-ray diffraction pattern measurements. The measurement was performed by using an X-ray diffratometer (Bruker, D8 Discover) that uses an X-ray tube (Cu).

Photoluminescence (PL) spectra and quantum yield

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*) This article is based on the presentation at the Conference on Laser Energy Science / Laser and Accelerator Neutron Sources and Applications 2017.

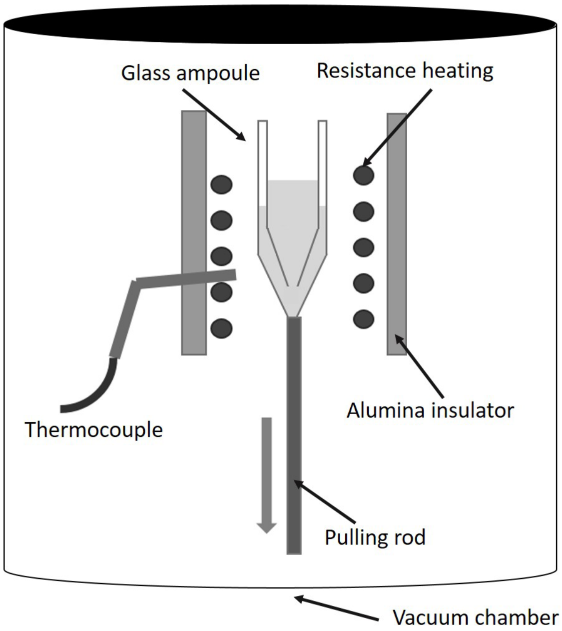

Fig. 1 Schematic diagram of SSVB method.

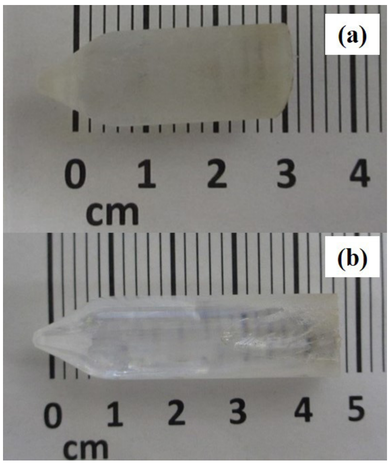

Fig. 2 The as-grown (a) trans-stilbene and (b) p-terphenyl crystals.

were evaluated using the absolute PL quantum yield measurement system (Hamamatsu, C9920-03). This system was composed of a spectral light source, an integrating sphere and a multichannel spectrometer. The sample was set in the integrating sphere and excited at 255 nm.

Radioluminescence spectra were recorded with a spectrometer (Edinburgh instruments, FLS920) under alpha-ray excitation source (^{241}Am isotope with energy of 5.5 MeV). Pulse height spectra were measured under the same alpha-ray excitation on the samples optically coupled with a photomultiplier tube (Hamamatsu, R7600). The signal was collected into a multichannel analyzer (Amptek, 800A) through pre-amplifier (ORTEC 113), and shaping-amplifier (ORTEC 556) (τ = 0.5 μs). Pulse height spectra were compared with conventional neutron Li-glass scintillator GS-20 (Applied Scintillation Technologies) used as a reference. The scintillation decay signals under neutron excitation (^{252}Cf) were repeatedly recorded from the signals of the PMT using an oscilloscope (Tektoronix, TDS 3052B). The decay time profiles were estimated as the average of these signals. All luminescence and scintillation characterizations were measured at the room temperature.

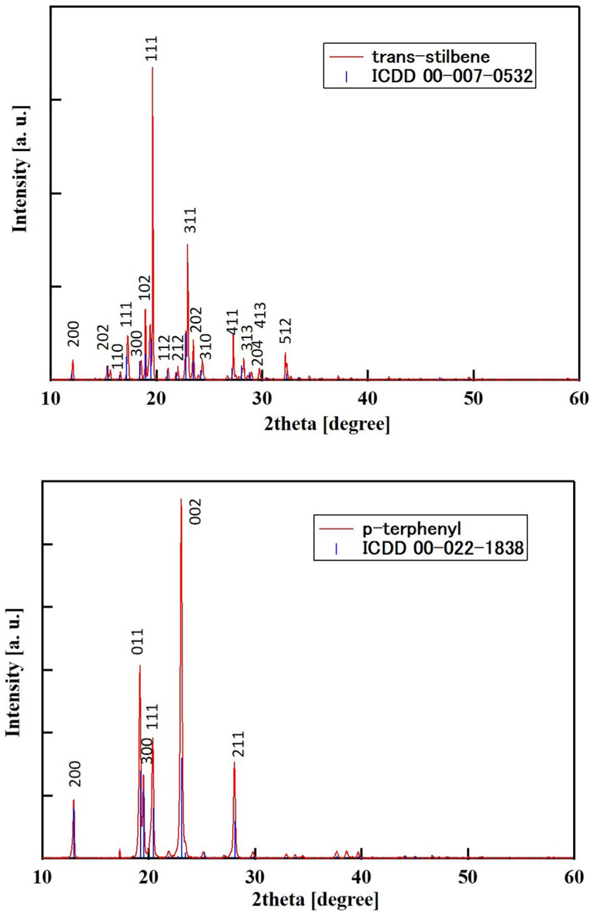

Fig. 3 Powder X-ray diffraction patterns of trans-stilbene (upper) and p-terphenyl (lower) single crystals.

3. Results and Discussion

As-grown single crystals of trans-stilbene and p-terphenyl prepared by the SSVB method are shown in Fig. 2. The diameter of grown crystals is 11 mm and they appeared transparent, however, the part in the last stage of p-terphenyl crystal shows pores. These pores might be generated due to temperature gradient in the radial direction at the growth front. Both crystals have the brown colored surface in the first and last stage due to presence of impurities. These parts were cut off and excluded from the specimens for luminescent property evaluations.

Powder X-ray diffraction patterns of grown trans-stilbene and p-terphenyl crystals are shown in Fig. 3. Their peaks are in good agreement with those of ICDD data (00-007-0532 and 00-022-1838). Other peaks derived from im-

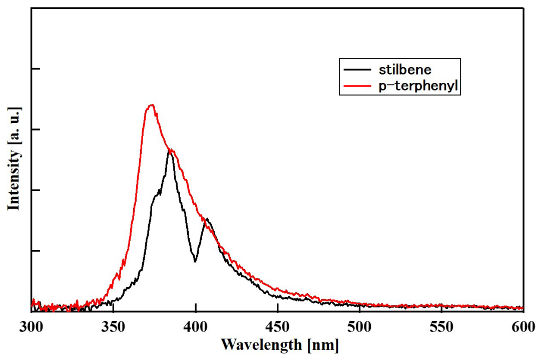

Fig. 4 Photoluminescence spectra of trans-stilbene and p-terphenyl under 255 nm excitation.

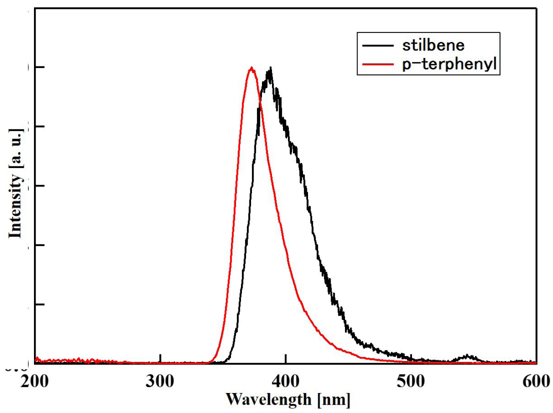

Fig. 5 Radioluminescence spectra of trans-stilbene and p-terphenyl under 5.5 MeV alpha-ray excitation.

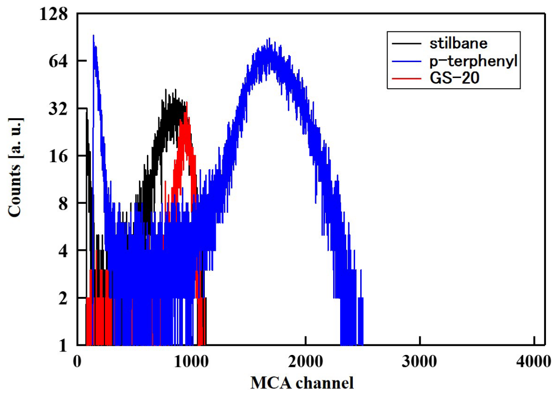

Fig. 6 Pulse height spectra of trans-stilbene and p-terphenyl crystals under 5.5 MeV alpha-ray excitation.

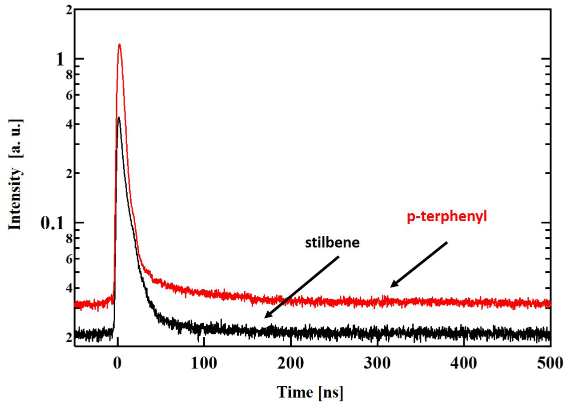

Fig. 7 Decay profiles of trans-stilbene and p-terphenyl under neutron irradiation.

purities are not detected in these measurements.

Photoluminescence spectra of trans-stilbene and p-terphenyl crystals under 255 nm excitation are shown in Fig. 4. Their quantum yields are 52.4% and 79.7%, respectively. Quantum yield is suppressed by chemical impurities, defects, and self-absorption. These values are similar to those of previous study using high purity materials [3].

Radioluminescence spectra of trans-stilbene and p-terphenyl under 5.5 MeV alpha-ray excitation are presented in Fig. 5. The trans-stilbene crystal has two intense peaks at 388 and 408 nm due to $S_1 \rightarrow S_0$ transition, and one weak peak at 545 nm due to $T_1 \rightarrow S_0$ transition [4]. On the other hand, the p-terphenyl crystal has one intense peak at 373 nm related to the $S_1 \rightarrow S_0$ transition. No other peaks of $T_1 \rightarrow S_0$ transition are observed.

Pulse height spectra of trans-stilbene and p-terphenyl crystals under 5.5 MeV alpha-ray excitation are shown in Fig. 6. The light yields are corrected for the position of 5.5 MeV alpha-ray full-energy peak considering the quantum efficiency of the photomultiplier tube. The light yields of trans-stilbene and p-terphenyl crystals are 0.89 and 1.80 times higher than that of GS-20, respectively.

Scintillation decay time profiles of trans-stilbene and p-terphenyl crystals under neutron irradiation are displayed in Fig. 7. The single exponential functions were used to fit the decay curves of trans-stilbene and p-terphenyl crystals obtaining values of 8.2 and 5.8 ns, respectively. These values are similar to those of previous study, however, in this work the instrumental response function is included [5]. In the future study, we will focus on evaluation of decay time more precisely using a fast decay measurement setup such as a streak camera.

4. Conclusion

Trans-stilbene and p-terphenyl crystals of 11 mm in diameter were successfully grown using SSVB method. Their photo- and radio-luminesce spectra were similar in the shape and peak positions to those of previous study. The quantum yield of trans-stilbene and p-terphenyl crystals was was 52.4% and 79.7%, respectively. The light yields of trans-stilbene and p-terphenyl crystals were 0.89 and 1.80 times higher than that of GS-20 standard, respectively. Their scintillation decay times were in nanosecond range and similar to those of previous study reaching values of 8.2 and 5.8 ns, respectively. In the future work, the temperature dependence of scintillation properties and more precise evaluation of scintillation decays is going to be performed.

Acknowledgments

This work is partially supported by (1) Japan Society for the Promotion of Science (JSPS) KAKENHI Grant Number JP16818695 and (2) Japan Science and Technology Agency (JST), Adaptable & Seamless Technology Transfer Program through Target-driven R&D (A-STEP), Grant Number AS272I010c (15667421).

[1] K. Shibata *et al.*, "Japanese Evaluated Nuclear Data Library Version 3 Revision-3: JENDL-3.3", J. Nucl. Sci. Technol. **39**, 1125 (2002).
[2] A. Arulchackkar avarthi *et al.*, J. Cryst. Growth **234**, 159 (2002).
[3] R. Kato *et al.*, J. Phys. Chem. C **113**, 2961 (2009).
[4] N.P. Zaitseva *et al.*, Proc. SPIE **7449**, 744911 (2009).
[5] R.C. Sangster *et al.*, J. Chem. Phys. **24**, 670 (1956).