Journal of Crystal Growth 310 (2008) 4468–4471

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Growth and optical properties of large single crystals of rhodamine from methanol solution

Marziale Milani [a,c,*], Federica Causa [b], Lorenzo Ferraro [a,c]

[a] Department of Materials Science, University of Milano-Bicocca, Via Cozzi 53, 20125 Milan, Italy
[b] Department of Electronic and Electrical Engineering, University of Bath, Bath BA2 7AY, UK
[c] Laboratory FIB/SEM 'Bombay', University of Milano-Bicocca, Via Cozzi 53, 20125 Milano, Italy

ARTICLE INFO

Article history:
Received 15 May 2008
Received in revised form
16 July 2008
Accepted 28 July 2008
Communicated by K. Sato
Available online 12 August 2008

PACS:
41.75.Ak
68.37.Vj
42.70.Mp
61.66.Hq
42.70.Hj

Keywords:
A2. Growth from solutions
A2. Single crystal growth
B1. Organic compounds
B3. Nonlinear optical

ABSTRACT

We report for the first time the existence of large-size (more than 1 mm in length) rhodamine (RH6G) crystals. The newly discovered structure of such crystals obtained with X-ray diffractometry is presented. The crystal is birefringent and can be imaged non-destructively using X-ray, electron and ion beam techniques.

1. Introduction

Rhodamine is a dye, an organic molecule well-studied in laser physics and nonlinear optics for its fluorescent properties [1–3]. Solutions of this dye are commonly used in biology as a staining fluorescent dye for optical microscopy and in optical applications to provide laser gain media. Dyeing of crystals is a practice that was developed particularly for quantum optics applications [4], because of the very significant increase in surface area achieved in *growing* crystals, and for photonics to obtain direct or inverted opals [5].

Rhodamine crystals grown from solution have been widely reported in the literature, e.g., Ref. [4], to be of typical size less than 5 μm. In this paper we report the successful growth of macroscopic size crystals, of length of the order of 1 mm, starting from a rhodamine 6G solution with methanol. This success opens up the possibility of utilizing such crystals as optically active elements that can be coupled with optoelectronic devices (such as light-emitting diodes, superluminescent diodes and semiconductor lasers) emitting in the violet–ultraviolet range for a wide range of applications.

2. Materials and methods

A slightly supersaturated solution (10^{-3} M) of rhodamine 6G (rhodamine 590 chloride from Exciton, Inc., Dayton, Ohio) in methanol was prepared and stored in a 4 ml quartz cuvette for spectrophotometry, with 1 mm × 1 mm square section and 10 mm length. The cuvette was then sealed with a Teflon cap, and exposed to nitrogen laser pulses at 337 nm for about 100 pulses (equivalent to ~100 mJ) [6]. The cuvette was kept in the dark at room temperature for 6 months. After this time lapse seven large crystals were present in the cuvette, while the total suspension volume was reduced to 3 ml by gas permeability of the Teflon cap.

* Corresponding author at: Department of Materials Science, University of Milano-Bicocca, Via Cozzi 53, 20125 Milan, Italy. Tel.: +39 02 64485175; fax: +39 02 64485400.
E-mail address: marziale.milani@unimib.it (M. Milani).

0022-0248/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2008.07.120

Structure analysis of such crystals was performed using a SMART-APEX (Bruker) diffractometer.

A dual beam system (Quanta 3D, FEI) was used for FIB/SEM operation. The ion beam resolution was 10 nm at 30 kV and 1 pA current. The accelerating voltage covers the range 5–30 kV. Thermal-emission SEM with dual-anode source emission geometry, fixed objective lens final aperture and through-the-lens differential pumping was used for further high-resolution imaging (3.5 nm, with 30 kV accelerating voltage in high vacuum).

Rough milling was used to operate a cut in one of the crystals (ion currents of 5–7 nA at 30 kV accelerating voltage, 1 μs dwell time and 50% overlap, corresponding to 100–150 nm ion beam

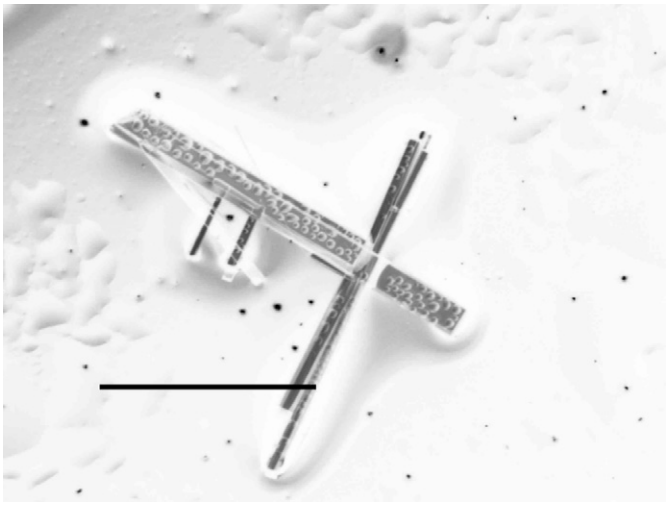

Fig. 1. Optical microscopy image of one of the crystals in solution (bar: 1 mm).

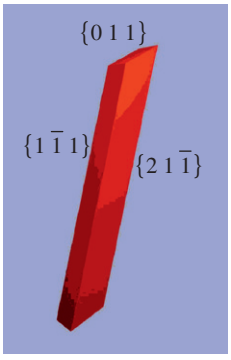

Fig. 2. Crystal habit with indexing of faces.

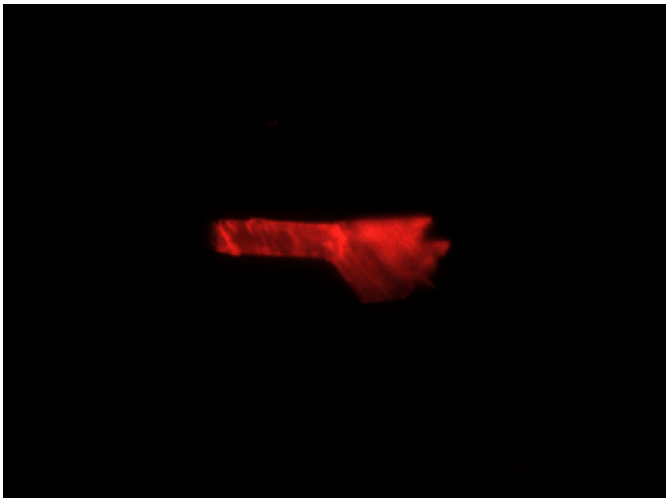

Fig. 3. Photo-excitation response of in-house-grown rhodamine crystal. Pumping optical signal at 365 nm; detected at 590 nm. The exposure time is 180 ms.

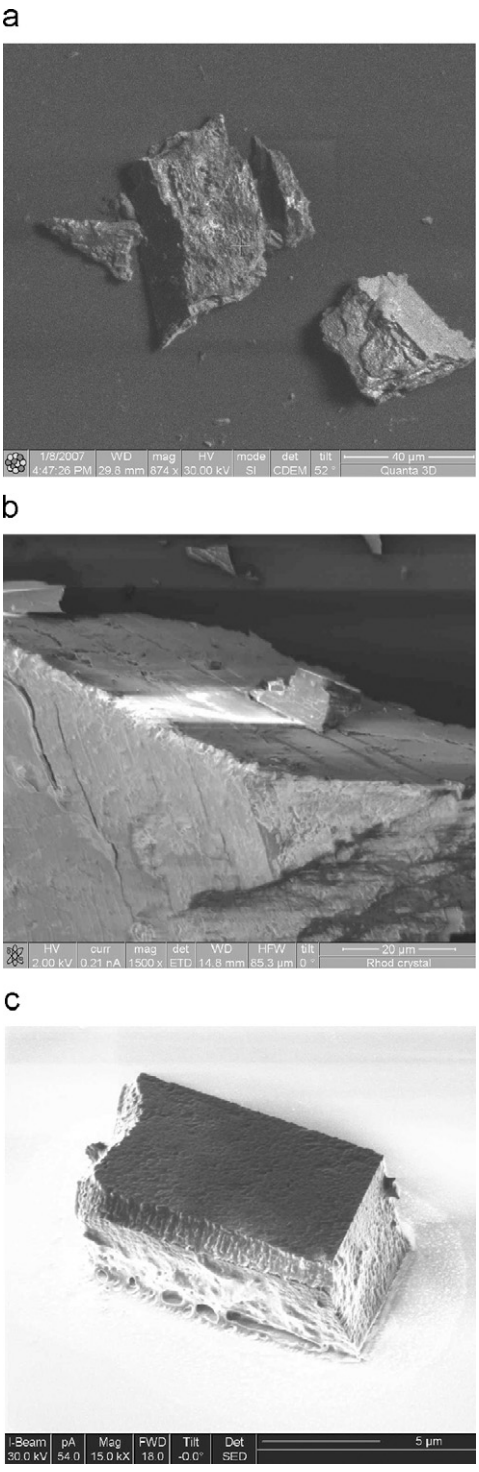

Fig. 4. FIB imaging of the in-house-grown rhodamine crystal: (a) ion imaging of a crystal portion (ion acceleration: 30 kV, 874 ×, detector: SI-CDEM); (b) secondary electron imaging of a crystal portion (electron acceleration: 2 kV, 1500 ×, detector: ETD); and (c) ion imaging of a small-size rhodamine crystal as grown (electron acceleration: 30 kV, 15k ×, detector: SED), showing the high quality of the crystal facets.